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A novel method for preparing electrospun fibers with nano-/micro-scale porous structures

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Abstract Electrospun fibers with nano-/micro-scale porous structures were successfully fabricated from polymer solutions that contained suspended micro-/nano-size salt particles of sodium chloride or calcium carbonate, which were subsequently removed through a leaching process after electrospinning. It was found that the size and dispersion of the salt particles had significant effects on the pore size and pore distribution in the resulting electrospun fibers. Using sodium chloride salt particles in the electrospinning process should not induce any residual toxicity in the resulting porous fibers. Therefore, this approach provides a very simple and versatile method in the fabrication of electrospun fibers that have secondary nano-/micro-scale porous structures, which are desirable in many important biomedical applications including tissue engineering and controllable drug release.

Keywords Electrospinning · Nanofibers · Nanotechnology · Porous structures · Poly (ε-caprolactone) · Salt leaching

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Introduction

Since it was first introduced in 1930 with an electrospray [1, 2], electrospinning has become a simple, versatile, and useful technique for fabricating nanofibers from a rich variety of functional materials. In a typical procedure, a high voltage is applied to a metallic spinneret, which is connected to a reservoir holding a polymer solution with proper viscosity, conductivity, and surface tension. Recently, significant progress has been made in producing nanofibers with special secondary structures, core/shell nanofibers [3, 4], hollow nanofibers [5], as well as porous nanofibers [6].

By virtue of a high surface area to mass ratio, nonwoven electrospun fiber mats have offered potentially advantageous performance in the fields encompassing tissue engineering to membrane science [6]. The surface area of a solid nanofiber can be further significantly increased by introducing a porous structure. Increase in surface area is beneficial and important to many applications, which include catalysis, filtration, absorption, fuel cells, solar cells, batteries, drug delivery and tissue engineering [7]. For instance, porous surfaces can provide more binding or adsorption sites for drug loading. In addition, introduction of porous structures modifies the fiber surface properties such as morphology and wettability, which can also influence cellular adhesion and interactions with the scaffold materials in tissue engineering applications.

The surface morphology of electrospun polymer fibers is governed by several electrospinning parameters, which include the applied electrical voltage, solution ejection rate, phase diagram, and polymer solution properties such as viscoelasticity, spinnability, temperature, and competition between the rates of phase separation and solvent evaporation [8, 9]. At present, use of phase separation of different polymers during electrospinning with proper spinning parameters has been one of the most important approaches for preparing porous electrospun fibers [10–12]. Dayal's study [6] demonstrated that the competition between phase separation rate and evaporation rate of solvents played a key role in producing porous structures in the resulting fibers. Such a phase separation method for producing porous structures requires a complicated organic solvent system (usually more than two solvents) to adjust the rates of phase separation and solvent evaporation. Use of multiple solvents increases additional potential risk of destroying drug activity. It should also be noted that not all materials can be dissolved into an appropriate solvent to form a solution for electrospinning. It is very difficult to properly adjust the rates of phase separation and solvent evaporation in order to produce electrospun fibers with desired porous structures. The aforementioned limitations of such a method have resulted in a very limited selection of polymers and drugs in potential applications.

In this communication, we report one simple and versatile technique that was developed for producing porous fibers based on the selective removal of a component from electrospun nanofibers made of a composite or blend materials. In this method, polymer solutions that contained nano-scale size salt particles were directly electrospun into polymer fibers; electrospun fibers with nano-/micro-scale porous structures were then obtained via leaching the salt particles out of the resulting fibers.

Experimental

The experiment involved the use of Poly (ε-caprolactone) (PCL), an aliphatic polyester that has frequently been used for biomedical and tissue engineering applications. PCL was dissolved and the salt particles were dispersed in a solvent mixture of chloroform and methanol by both mechanical agitation and ultrasonication to obtain a PCL solution with a stable suspension of the salt particles. The solution was then placed in a syringe and supplied using a syringe pump. Electroconductive templates were employed as the collectors for the electrospinning process. The resulting PCL/salt particle composite fibers were subsequently immersed in an appropriate solvent to leach the salt out.

Materials

PCL, which has an average molecular weight (MW) of 80 kDa, was purchased from Aldrich (USA). Sodium chloride salt particles ($\leq$1 μm), chloroform and methanol of analytical grade were purchased from Fisher scientific (USA). Calcium carbonate nanoparticles with particle-size $\leq$100 nm were purchased from American Element (USA).

Electrospinning

PCL was dissolved in a mixture of chloroform and methanol (3:1 by volume) to prepare a 9 wt% solution. Sodium chloride microparticles or calcium carbonate nanoparticles were added to the PCL solution and stirred for 2 h, and then ultrasonically treated for 2 min to achieve uniform dispersion and stable suspension. The spray rate of the PCL solution from the syringe was controlled at 0.025 mL min^{-1} by using a syringe pump. The voltage applied to the needle of the syringe was 20 kV and the distance between the needle tip and the collector was 9 cm.

Salt leaching

The leaching of sodium chloride particles from electrospun PCL fibers was performed using DI water, and the leaching of calcium carbonate nano-particles was done with 2 M hydrochloric acid (HCl) aqueous solution.

Fiber surface examination

The resulting electrospun fibres were first coated with platinum in a sputtering coater. The fiber surfaces were examined with scanning electron microscopy (SEM) (Hitachi S4700 Field Emission Scanning Electron Microscope) at an accelerating voltage of 5 kV.

Results and discussion

Two representative SEM images of these electrospun PCL fibers are shown in Fig. 1. It can be seen that two types of porous structures were obtained on the

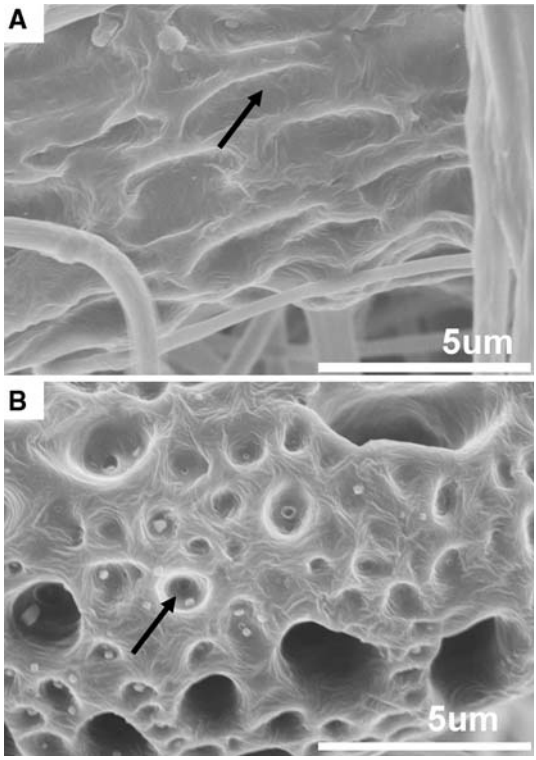

Fig. 1 The SEM image of two typical porous structures existing on the resulting electrospun PCL fibers after leaching out the salt particles

resulting electrospun fibers after salt leaching. One is a groove shape, shown in Fig. 1a, in which a majority of the grooves stretched to several micrometers. Another includes pore shapes with sizes ranging from several hundred nanometers to several micrometers as shown in Fig. 1b. From Fig. 1, it was also noted that the diameter of electrospun fibers has a very broad distribution from nano- to micro-scale, and only the larger diameter fibers possess secondary porous structures. The reason for this is that the salt microparticles are difficult to cover or attach onto the surface of small diameter fibers due to the larger size of salt particles ($\leq$1 μm) during the electrospinning process.

In order to obtain the secondary porous structures on small diameter fibers, nano-particles of calcium carbonate ($\leq$100 nm) were suspended in PCL solution with the aid of ultrasonication to achieve a stable particle suspension. The typical images of the electrospun fibers thus prepared are shown in Fig. 2b, c, and d. Figure 2a shows the control of PCL nanofibers with smooth surfaces electrospun from PCL solution without nanoparticle addition. From Fig. 2b, it can be clearly seen that the secondary pores and grooves were obtained on PCL nanofibers with addition of calcium carbonate nano-particles into the PCL solution. The SEM images of PCL/calcium carbonate nano-particle composite fibers taken before (Fig. 2c) and after (Fig. 2d) salt leaching demonstrated that small diameter fibers were obtained by adding nanoparticles into PCL solutions. It was also noticed that the nanoparticles

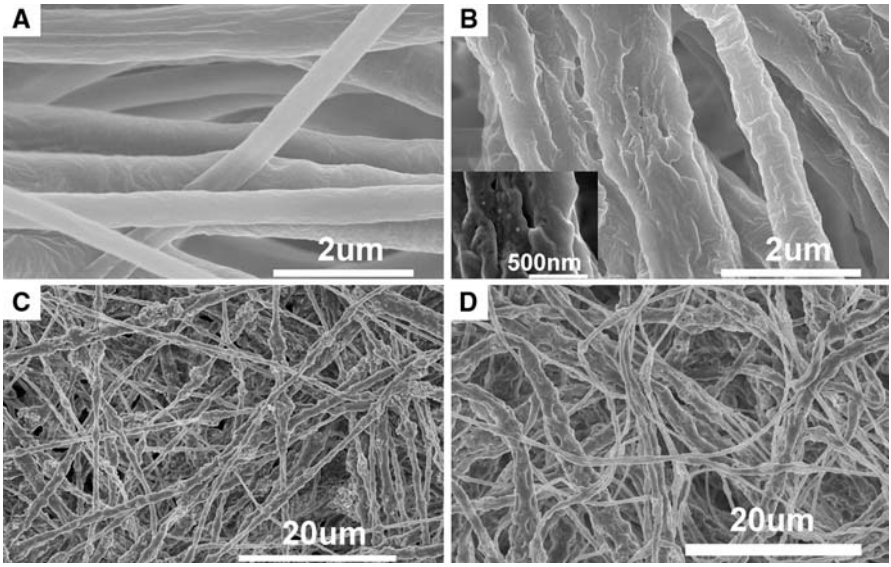

Fig. 2 SEM images of: **a** the smooth surface of non-porous structures on PCL fibers electrospun from a PCL solution without salt particle addition; **b** the surface morphology of porous electrospun PCL fibers, **c** the electrospun fibers before salt leaching, **d** the electrospun fibers after salt leaching

aggregated to some extent during mixing and could not be completely dispersed in solution, which resulted in the larger pores and non-uniformity of the porous structure on nanofiber surfaces as shown Fig. 2d. In other words, both salt particle-size and dispersion uniformity had significant effects on the pore sizes and distributions of the electrospun fibers. These results indicate that uniform dispersion and stable suspension of nanoparticles in a polymer solution are necessary in order to fabricate electrospun fibers with uniform porous structures. In this study, although ultrasonication was used for nanoparticle dispersion, the suspension stability of salt nanoparticles in polymer solutions needs to be improved in order to produce electrospun fibers with uniform pores and pore size distribution. Use of a hybrid twin screw extrusion/electrospinning technique, as demonstrated by Erisken et al's studies [13, 14], could be one remedy to the problem of controlling the dispersion stability of particles and nanoparticles in polymer solutions during the electrospinning process.

The SEM images of the as spun nanofibers show in Fig. 3a indicate that the calcium carbonate nano-particles were not embedded inside electrospun PCL fibers, and most of the nanoparticles were just attached onto the fibers' surfaces. During the leaching process, the particles were easily dissolved and removed by HCl, and nano-porous structures were left on the fibers' surfaces as shown in Fig. 3b. Figure 3c shows the weight loss curve of the calcium carbonate nanoparticles as a function of leaching time. It can be seen that the calcium carbonate nano-particles can be almost completely removed (94.25%) after leaching for 2 h in a 2 M HCl aqueous solution.

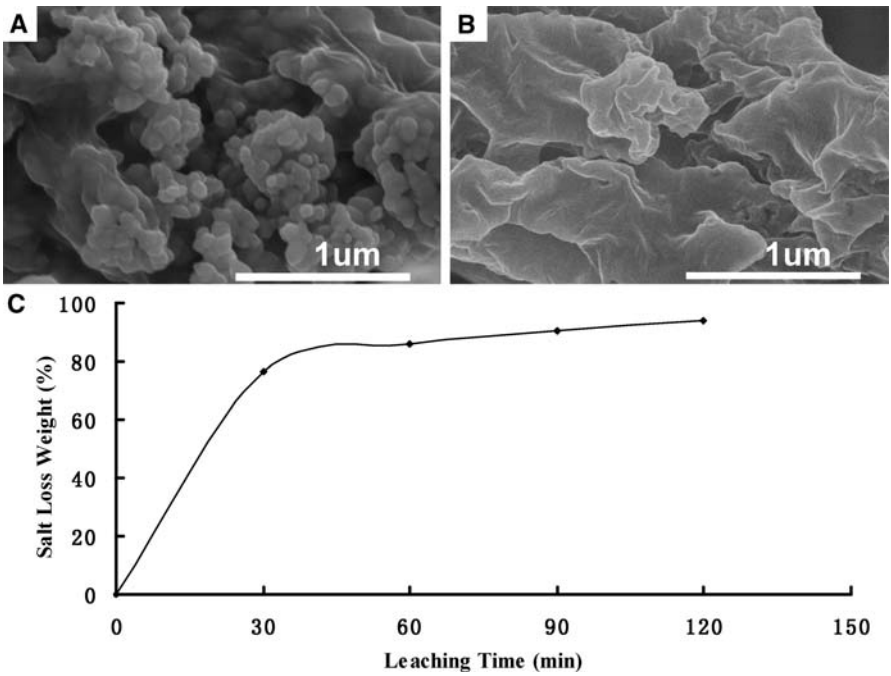

Fig. 3 SEM images of: **a** $CaCO_3$ nanoparticles distributed on the surface of electrospun fibers before leaching; and **b** the porous structures of electrospun fibers after salt leaching. **c** the weight loss curve of the electrospun PCL fibers from a 9.0 wt. % PCL solution with salt addition (PCL:$CaCO_3$ = 1:1 by mass ratio) as a function of leaching time in a 2 M hydrochloric acid aqueous solution

Conclusions

Electrospun fibers with nano-/micro-scale porous structures were successfully fabricated from polymer solutions that contained micro-/nano-sized salt particles via electrospinning and a subsequent salt leaching process. It was found that both the size and dispersion of salt particles in a polymer solution had significant effects on the size and distribution of the porous structures on the electrospun fibers. When sodium chloride salt particles were used, it should not introduce any residual toxicity on the porous fibers. Therefore, this approach provides a very simple and versatile method in fabrication of electrospun fibers that have secondary nano-/micro-scale porous structures, which are highly desired for many important biomedical applications such as tissue engineering and controllable drug release.

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