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NANOFIBROUS MATS WITH BIRD'S NEST PATTERNS BY ELECTROSPINNING*

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Abstract Electrospun material with bio-inspired ordered architectures and patterns is very interesting, yet remains a challenge. We report here that nanofibrous mats with bird's nest patterned structures can be directly electrospun from chlorinated polypropylene solutions doped with an ionic liquid. The solution viscosity and the ionic liquid content are two dominant factors to influence the topological morphology of the nanofibrous mats. The patterned structures can be further modulated by the collection time of electrospinning, the humidity of environment and the design of collector. We suggest the electrostatic repulsion between the residual charges of the mat surface and the upcoming nanofibers plays a key role in the formation of the bird's nest patterns.

Keywords: Electrospinning; Ionic liquid; Patterned structures.

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INTRODUCTION

In view of the oceans of time that nature has had to optimize and perfect itself, it is not surprising that biomimicry is one of the most rapidly growing research fields, especially for material scientists. Based on various biomimicry approaches, a series of advanced materials with bio-inspired structures have been developed in recent years. The prominent advantage of bio-inspired structures is to make the most economical use of materials to achieve optimized performances, while an important feature is that they usually have ordered or patterned construction. One of these bio-inspired structures is the historical landmark for the Olympics of 2008 — Beijing National Stadium. In this landmark, the structural elements mutually support each other and converge into a grid-like formation. It is almost like a bird's nest with its interwoven twigs, so its nickname is 'Bird's Nest'. Such a bio-inspired structure ensures that the high rise building is strong enough to withstand an earthquake (Grade 8–9) and go through all the vicissitudes just as birds do.

Various technologies have been explored to construct ordered or patterned structures for advanced materials. Electrospinning has been preliminarily demonstrated as a simple and versatile method for this purpose. For example, Xia *et al.* have reported that by introducing a gap into a conventional plate collector, uniaxially aligned nanofibers over large area can be electrospun[1]. They have also indicated that the area and geometric shape of the insulating gap have effects on the ordered deposition of nanofibers[2]. Zhang *et al.* have prepared electrospun mats with patterned architectures using electroconductive templates (a woven wire fabric), and showed that protrusions in the collector are important parameters[3]. This method has also been developed

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by Zhang, and Chang to achieve patterned organization on nanofibrous tubes[4]. More recently, Ziaie *et al.* have reported the selective deposition of nanofibers on an elastomeric substrate with gold-coated pyramidal protrusions and indicated this technique as 'field-enhanced electrospinning'[5]. Star and radial fiber patterns have also been prepared by using enamel-coated steel sheets as collector[6]. The central points here are to change the electric field distributions and control the jet path during the electrospinning process. Ramakrishna *et al.* have comprehensively reviewed the electrospinning setups and processes that can be used to fabricate ordered nanofibers[7]. Alternatively, precisely defined microarchitechures were available by combining electrospinning with microcontact printing or photolithographic process[8–11]. Despite the great progress researchers have made, however, approaches applied so far are not a panacea for the preparation of ordered or patterned structures, because complicated electrospinning setups or exquisite laboratory procedures are often required. In addition, the area of patterned structure is usually limited, thus preventing the massive preparation of desired nanofibrous mats.

Herein, we describe the preparation of a bio-inspired patterned structure of nanofibrous mats by one-step electrospinning. These patterned nanofibrous mats can be directly electrospun on a common plate collector when chlorinated polypropylene (CPP) or polystyrene (PS) in xylene/cyclohexanone (1:1 *V*/*V*) solutions were doped with an ionic liquid — 1-dodecyl-3-methylimidazolium hexafluorophosphate. Even more interesting is that such patterned structures are very similar to Beijing National Stadium-'Bird's Nest' at micron dimension (Fig. 1). Further studies indicate that it is possible for us to control the patterned structures by simply varying the electrospinning parameters.

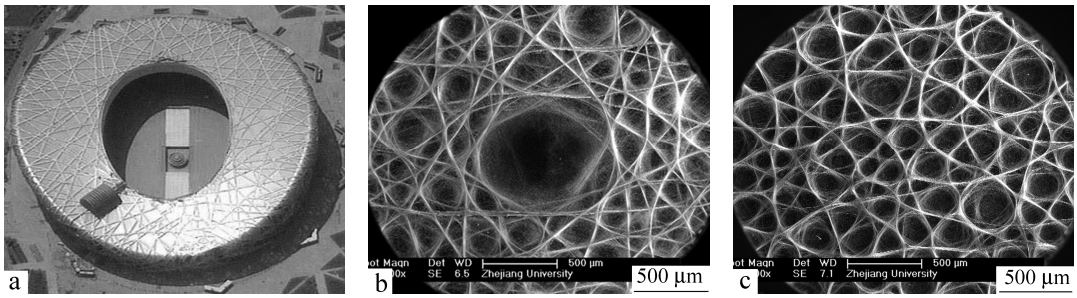


Fig. 1 Images of (a) Beijing National Stadium-Bird's Nest and (b, c) as-prepared electrospun nanofibrous mats

EXPERIMENTAL

Chlorinated polypropylene (CPP) was purchased from Hangzhou Juli Chemical Co., Ltd and purified by precipitating a 150 g/L xylene solution into a 10-fold excess of cold ethanol for 3 times before use. The chlorinated degree was about 30 wt% by elemental analysis (Flash EA 1112, ThermoFinnigan, USA). The number-average molecular weight determined by a Waters gel permeation chromatograph (GPC) system was 1.08×10^5 with a polydispersity 2.4. THF was used as the eluent and GPC standard polystyrene as the calibration standard. Polystyrene (PS, $M_n = 8.13 \times 10^4$, PDI = 2.89) was got from Zhenjiang Chi Mei Chemical Co., Ltd and used without purification. 1-Dodecyl-3-methylimidazolium hexafluorophosphate [C12Mim]·[PF6] (purity > 95%) was supplied by Lanzhou Greenchem ILS, LICP, CAS and used without further treatment. Xylene, cyclohexanone and ethanol were of analytical grade and used as received.

An electrospinning solution was prepared by dissolving certain amounts of CPP or PS and [C12Mim]·[PF6] in xylene/cyclohexanone (1:1 *V*/*V*) mixed solvent for at least 5 h at 60°C with gently magnetic stirring. Different samples were assigned as CPP A+B or PS A+B according to the solution compositions. Taking CPP 18 + 15 as an example, this means there was 180 g/L CPP in the solution, and the relative weight content of [C12Mim]·[PF6] to CPP was 15 wt%. After removing the air bubbles completely, the solution was transferred into a plastic syringe (20 mL) and electrospinning was performed with following conditions: applied voltage 9.5 kV, flow rate 0.5 mL/h, tip-to-collector distance 15 cm, diameter of stainless steel needle 1.2 mm, room

temperature. The electrospinning process was conducted in an enclosed chamber, in which the relative humidity could be controlled by dehumidifier/steam humidifier from 35% to 80%.

The viscosity and conductivity of polymer solutions were measured with a TA AR-G2 steel cone rheometer (cone angle 2^{o}, D = 40 mm) at 25^{o}C and a conductivity meter (FE30, Mettler Toledo, Switzerland). Field emission scanning electron microscopy (FESEM, SIRION-100, FEI, USA) was employed at 25 kV to study the morphology of the bird's nest patterned nanofibrous mats after samples were sputtering coated with gold.

RESULTS AND DISCUSSION

It is well known electrospinning polyolefins into nanofibrous mats is relatively difficult because these polymers can not be dissolved in polar solvents. Polyolefin solutions from non-polar solvents usually have low dielectric constant and poor conductivity, which in turn result in poor electrospinnability. However, this hurdle can be overcome by just adding a small amount of ionic liquids, such as 1-dodecyl-3-methylimidazolium hexafluorophosphate ([C12Mim]·[PF6]). Ionic liquids are chosen here mainly because they have high electrical conductivity and their solubility properties can be easily modulated by changing one of the ions. As can be seen from Fig. 2, when pure CPP solution in xylene/cyclohexanone is adopted, there are only serious beaded-fibers on the collector (Fig. 2a) and beads can not be eliminated by simply increasing polymer concentration. The formation of beaded-fibers is due to the low charge density of the polymer solution[12], which results in insufficient stretch of the jet during the whipping process. With the addition of [C12Mim]·[PF6], the fiber morphology changes from beaded-fibers to smooth nanofibers with an average diameter of about 230 nm (Fig. 2b to 2d). This improvement of electrospinnability should be mainly ascribed to the increased conductivity of the polymer solution. The viscosity varies a little while the conductivity increases about 350 times from (0.105 ± 0.007) μS/cm to (37.53 ± 2.203) μS/cm when 10 wt% ionic liquid was added (Fig. 3). It is particularly interesting that there are some unanticipated patterns similar to bird's nest structure in the nanofibrous mats from a solution of 180 g/L CPP doped with 10 wt% [C12Mim]·[PF6] (designed as CPP 18+10, see experimental section) (Fig. 2c). Furthermore, these structures are reproducible and their appearance is not a coincidence themselves.

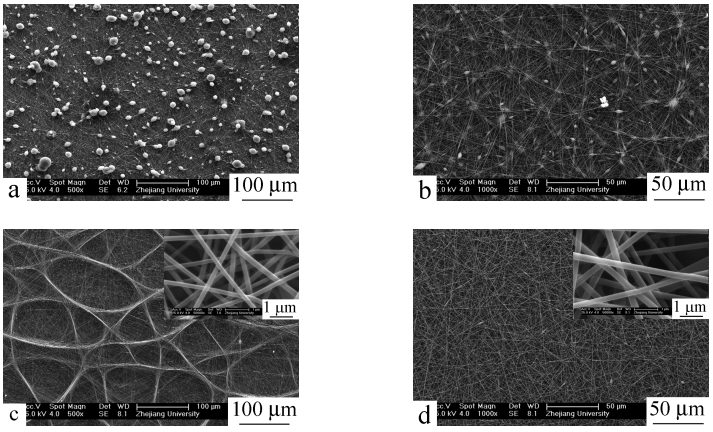


Fig. 2 SEM pictures of the nanofibrous mats electrospun from CPP solutions with different ionic liquid content: (a) CPP 18+0, (b) CPP 18+5, (c) CPP 18+10 and (d) CPP 18+15
The collection time is 20 min and relative humidity is 50%.

A combinatorial study of various solutions with different CPP concentrations and ionic liquid contents was conducted to correlate the solution property with the formation of patterned structures (Table S1 in supplementary material). Accordingly, three different topological morphologies can be obtained: patterned structures with beaded-fibers, patterned structures with uniform nanofibers and common mats with uniform nanofibers (Fig. 4). The formation of beaded-fibers at low CPP concentrations is due to the insufficient density

of chain entanglement even when the conductivity of polymer solution is high enough[13]. We note that the nest structure is a little parallelism to the dimpled structure reported by Ramakrishna *et al*.[14] and the honeycomb structure described by Deitzel *et al*[15]. However, the dimpled and honeycomb structures were mainly composed of polymer beads. The authors attributed these structures to the build-up of electrostatic charges on the deposited collectors. This conclusion seems reasonable when polymer solutions with low dielectric constant and poor conductivity are electrospun. The as-prepared nanofibers would carry residual charges after deposition on the collector, and previous studies have showed that the surface potential is as high as 300 V within 5 min electrospinning[5]. In our cases, the ionic liquid has intrinsic good conductivity and as its content is increased beyond a critical threshold value, the electrospun nanofibers should have good conductivity and the static-charge accumulation is reduced or even eliminated[16]. However, for the nanofibers with low ionic liquid content, they would behave like electrically insulating substrates and the charge accumulation is unavoidable. We also found that the critical ionic liquid content value decreased as the CPP concentration increased. It is because the fiber diameter increases exponentially with the polymer concentration which would promote the discharge process.

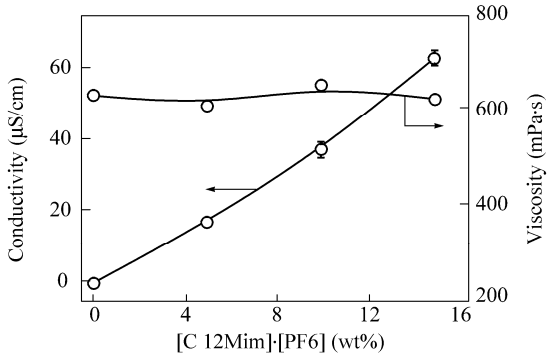


Fig. 3 Conductivity and viscosity change of 180 g/L CPP solution with content of [C12Mim]·[PF6]

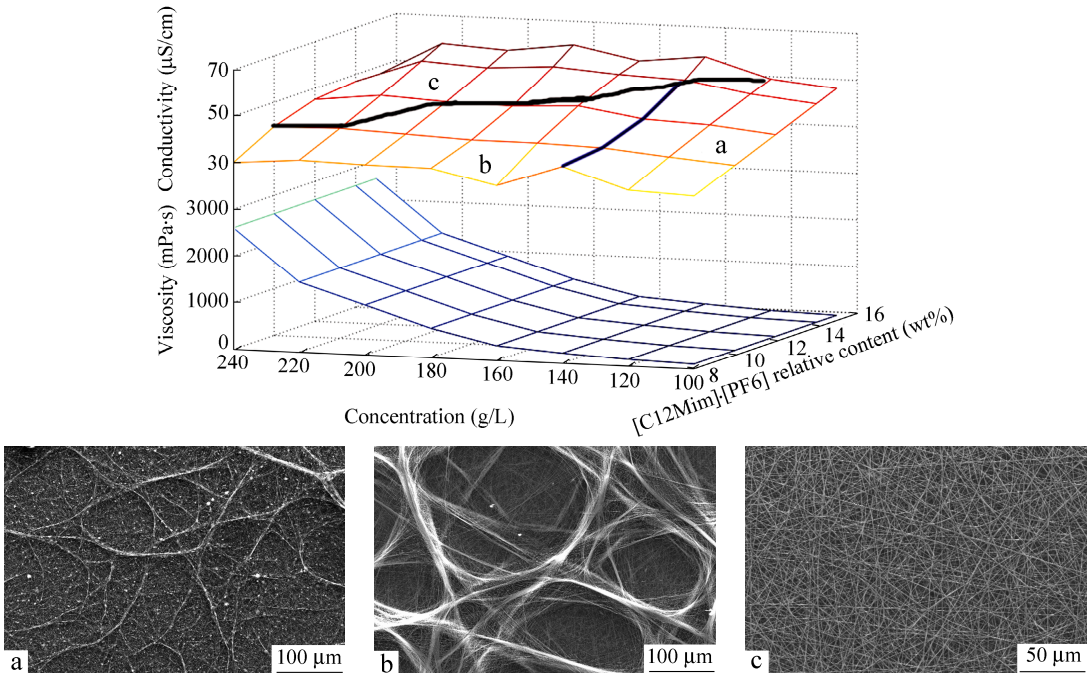


Fig. 4 Characteristics of CPP solutions and their influences on the topological morphology of CPP nanofibrous mats: (Zone a) patterned structures with beaded-fibers, (Zone b) patterned structures with uniform nanofibers and (Zone c) common mats with uniform nanofibers

The bird's nest patterned structures are mainly composed of nanofibrous bundles as the nest walls. A possible mechanism to account for the aggregate nanofibers with ionic liquid doped solutions has been proposed by Heiden *et al.*: negative charge is drawn back through the positively charged jet, so that these nanofiber segments begin to have excess negative charge; those segments closer to the needle with excess positive charge are drawn first towards the negatively charged nanofiber segments before hitting the collector as the collector repels them at the same time. They call this process 'backbuidling' [17, 18]. Here, besides the nanofiber bundles (Fig. 5a), some conjoined nanofibers (Fig. 5b) can also be found and it is particularly interesting to note that there exist twisted nanofibers (Fig. 5c). Yet no branched nanofibers can be found here, demonstrating that the nanofibers are completely dry when they meet each other and the 'backbuilding' process happens very near the collector. Moreover, the patterned structures vanish when the applied voltage increases to 11 kV (Fig. S1 in supplementary material). A possible reason is that, at high voltage, the electrospinning speed is so high that the nanofibers do not have enough time to 'backbuild' before arriving at the collector.

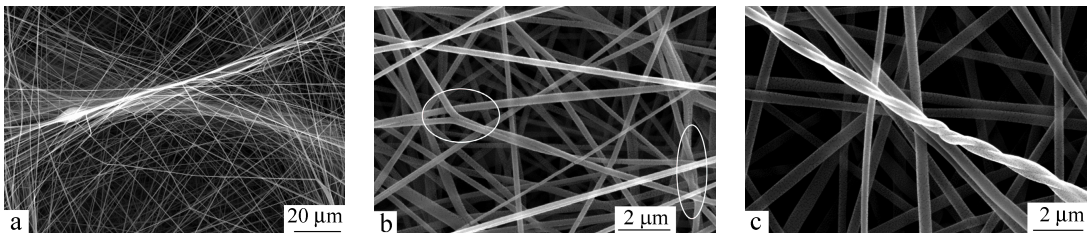


Fig. 5 (a) Nanofibrous bundles, (b) conjoined and (c) twisted nanofibers in the nanofibrous mats

To further demonstrate the formation mechanism of the patterned structures and to regulate them, various processing parameters which would influence the charge accumulation were taken into consideration. Taking CPP 18+10 as an example, their effects on the topological morphology of as-prepared mats were examined. Figure 6 displays the representative images of CPP/[C12Mim]·[PF6] nanofibrous mats collected on aluminum plate over six different periods of time. A whole procedure for the formation of patterned structures can be observed. Obvious changes occur in the surface morphology of the nanofibrous mats with collection time. At the very beginning, there are only some smooth nanofibers (Fig. 6a). Then bundles start to appear (Fig. 6b). At 5 min, some patterned structures form and their construction is similar to the bird's nest at micron dimension (Fig. 6c). As the collection time further increases, the bird's nest structures become more and more obvious (Figs. 6d, 6e). When the electrospinning is continued for 180 min, the bird's nest patterned structures are even observable with naked eyes (Figs. 6f, 6g). The explanations are as follows: at first only a few fibers spread on the plate and the charges on the nanofibers can be easily dissipated through the grounded aluminum foil. When a uniform thick layer of nanofibers is deposited, surface discharging becomes less efficient and positive charges start to accumulate on the nanofibrous mats. Liompart *et al*. calculated the charge saturation value of electrically insulating substrates and implied that there did have a critical substrate thickness S^* beyond which non-uniform collection would happen[19]. Then bundles and bird's nest structures begin to appear. Eventually, the bundles build up enough electrostatic charges to prevent nanofibers from lying directly on the mats, most of the nanofibers form new bundles and few are suspended slightly above the nest, leading a patterned structure to form[15].

Further, the electrospinning process was conducted at different relative humidity (Table 1). High relative humidity results in large fiber diameter as water induces the precipitation of polymer jet[20] and water in the air promotes the discharge process[14], both of them help to reduce charge accumulation. As expected, for CPP 18+10, at low (Fig. 7a) or middle relative humidity (Fig. 7b), the patterned structures exist. When relative humidity is up to 75%, the patterned structures disappear (Fig. 7c). There is a negative correlation between the ionic liquid content and the critical relative humidity. When the ionic liquid content increases to 12%, the critical relative humidity decreases to 55%. As the ionic liquid content is further raised up to 15%, only nanofibrous mats with uniform topological morphology appear at whatever relative humidity.

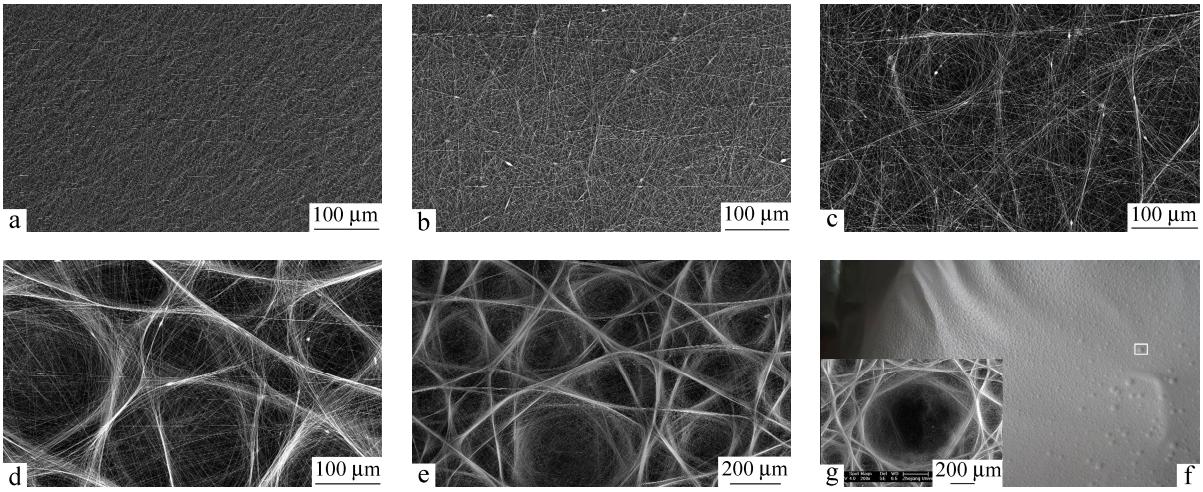


Fig. 6 Effects of collection time on the topology structure of the nanofibrous mats: (a) 1 min, (b) 3 min, (c) 5 min, (d) 20 min, (e) 60 min, (f) 180 min, (g) close-up view of the small rectangle in (f)
Relative humidity is 50%.

Table 1. Effects of relative humidity on the electrospinning of CPP

Sample name	Relative humidity (%)	Fiber diameter (nm)	Membrane morphology
CPP 18+10	45	221 ± 26	Bird's Nest
	55	284 ± 21	Bird's Nest
	75	341 ± 39	Nanofibers
CPP 18+12	45	237 ± 34	Bird's Nest
	55	266 ± 36	Nanofibers
CPP 18+15			Nanofibers

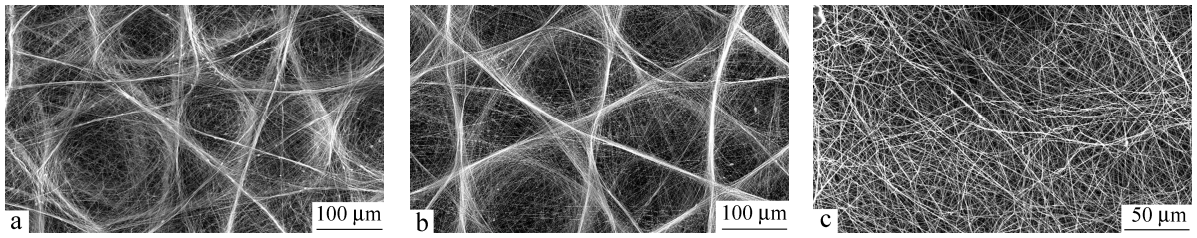


Fig. 7 SEM pictures of the nanofibrous mats electrospun from CPP 18+10 at different relative humidity: (a) 45%, (b) 55% and (c) 75%
The collection time is 20 min.

The formation of patterned structures can be promoted by using glass as non-conducting collector to enhance charge accumulation (Fig. S2 in supplementary material). Figure 8 shows the influence of collector configuration by putting a series of parallel grounded electrodes above the plate collector. For CPP 18+10, even when the collection time is as short as 3 min, some big holes can be found between air gaps besides aligned nanofibers and bundles (Fig. 8a). Meanwhile, for CPP 18+15, only aligned fibers can be obtained (Fig. 8c). The rapid formation of the so-called enlarged bird's nest patterned structures by simply introducing air gaps mainly results from the enhanced charge accumulation and strong repulsive interactions between suspended nanofibers[21, 22]. After a thick layer of nanofibers covers the air gaps completely at the central part, the surface morphology of mats is the same as that of plate collector (Figs. 8b, 8d). These visual results further confirm the role of surface residual charges. To sum up, patterned structures can be readily electrospun from ionic liquid doped CPP solution with appropriate viscosity and ionic liquid content at certain relative humidity, and those factors which enhance surface charge accumulation promote the formation of patterned structures, and vice-versa.

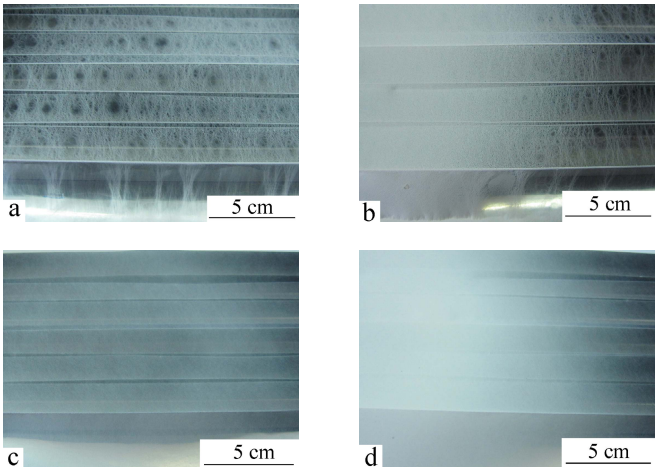


Fig. 8 Rapid formation of enlarged 'Bird's Nest' patterned structures by using parallel electrolodes as collector: (a) CPP 18+10, 3 min, (b) CPP 18+10, 20 min, (c) CPP 18+15, 3 min and (d) CPP 18+15, 20 min
Relative humidity is 50%.

Polystyrene was further tested to verify the universality of such bird's nest structures (Table S2 in supplementary material). The morphology of as-spun PS nanofibrous mats changes with the same trend as CPP (Fig. 9). Interestingly, bird's nest structures can also be electrospun from PS 18+10. However, this phenomenon does not work for PAN/DMF solution (541.42 mPa·s, (5.20 ± 0.06) μS/cm). These results arise from different polarities as PAN ($\varepsilon = 6.5$) is a polar polymer while CPP ($\varepsilon = 2.6$)[23] and PS ($\varepsilon = 2.5$) are non-polar polymers, which further influence the charge accumulation/ discharge process. It should be noted here that the selection of appropriate solvents is very important and solvent properties like conductivity, volatility and polarity may also have influence, as it is impossible to construct patterned mats from PS/DMF solution.

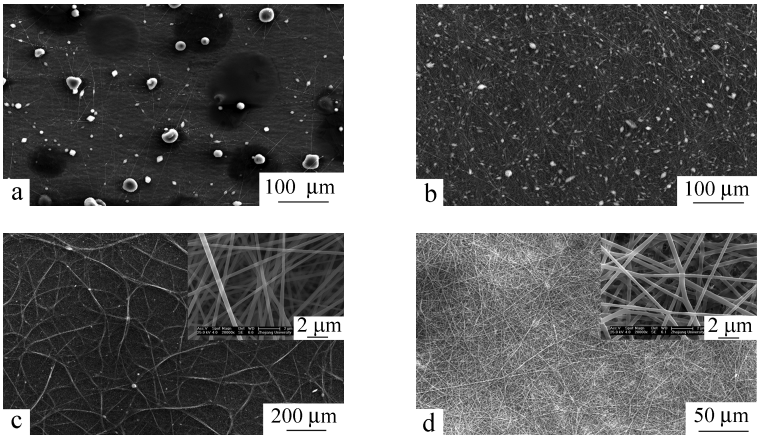


Fig. 9 SEM pictures of the nanofibrous mats electrospun from PS solutions with different ionic liquid contents: (a) PS 18+0, (b) PS 18+5, (c) PS 18+10 and (d) PS 18+15
The collection time is 20 min and relative humidity is 50%.

From what has been discussed herein, it suggests that charges accumulate on the collected mats with time; and the electrostatic repulsion between the residual surface charges of nanofibrous mats and the upcoming nanofibers results in the formation of nanofibrous bundles and patterned structures. However, the influence of the above discussed parameters may mutually be dependent, and the key parameters will be different in other electrospinning systems. The patterned mats having unique structure of bird's nest is endowed with promising

properties: the nanofiber bundles around the wall result in high mechanical strength, while filtration and air permeability are maintained in the nest regions[24]. Furthermore, considering that CPP and PS are very cheap industrial polymers, the as-prepared mats have potential application in air filtration field. Moreover, especially for biomedical applications, this method may be expanded to one-step construct patterned/non-woven hierarchical structures and the mats can be used as tissue regeneration scaffolds with functional-graded guidance. It has been previously reported that cells can be infiltrated into porous mats while remain on the surface of non-woven scaffold[25, 26].

CONCLUSIONS

In summary, nanofibrous mats with bird's nest patterns can be readily prepared by electrospinning chlorinated polypropylene and polystyrene in xylene/cyclohexanone (1:1 *V*/*V*) solutions doped with an ionic liquid under appropriate conditions. The formation procedure of the patterned structures can be viewed as an electrostatic repulsive interaction driven process. The electrostatic repulsion between the residual surface charges of as-prepared mats and the upcoming fibers plays a key role here. We believe that our work may provide a new method for preparing electrospun materials with patterned structures for applications in cell biology and air filtration.

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