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Electric field induced phase separation on electrospinning polyelectrolyte based core–shell nanofibers

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ABSTRACT

In the present study, we report a facile method to fabricate polyelectrolyte based core–shell nanofibers with the assistance of the high gradient electric potential between the tip of capillary and the collector. The core–shell structure and the composition of each layer have been supported by TEM and XPS studies. The effect of the electric field on the phase separation was considered to be the major factor. An electric field experiment was introduced to elucidate the influence of electric field on the phase separation process. It was assumed the polyelectrolyte based core–shell nanofibers membrane could be applied in wound care and tissue engineering.

1. Introduction

Electrospinning is considered to be the most convenient, economical and simplest technique for generating extremely long nanofibers (Caruso, Schattka, & Greiner, 2001; McCann, Li, & Xia, 2005; Yarin, 2011). Core–shell nanofibers as one of the most interesting nanostructures have attracted great attention due to a variety of special applications, including such field as biotechnology, drug delivery and nanofluidics (Dror et al., 2007; McCann et al., 2005; Yarin, 2011). To date several methods have been developed to fabricate core–shell structure of polymeric nanofibers, such as the fiber template method (Caruso et al., 2001; Qiu & Yu, 2008), the coaxial electrospinning method (Chan and Kotaki, 2009; Li and Xia, 2004a, 2004b) and the phase separation coelectrospinning process (Zhang et al., 2009; Zussman, Yarin, Bazilevsky, Avrahami, & Feldman, 2006). Electrospinning is considered to be a simple and promising technique for the production of core–shell fibers with diameters ranging from micro- to nanometer scale (Caruso et al., 2001; Li and Xia, 2004a, 2004b; McCann et al., 2005). In coaxial electrospinning, a plastic syringe with two compartments containing different polymer solutions is used to initiate a core–shell jet. At the exit of the core–shell needle attached to the syringe, a core–shell droplet appears, which acquires a shape similar to the Taylor cone due to the pulling action of the electric. Polymer solutions in the cone, being subjected to sufficiently strong (supercritical) electric field, issue a compound jet, which undergo the electrically driven bending instability characteristic of the ordinary electrospinning process. Strong jet stretching resulting from the bending instability is accompanied by enormous jet thinning and fast solvent evaporation. As a result, the core–shell jet solidifies and core–shell fibers are depositing on a counter-electrode (Caruso et al., 2001; Li and Xia, 2004a, 2004b; McCann et al., 2005; Yu, Fridrikh, & Rutledge, 2004).

However, it was recently demonstrated that core–shell structure polymeric nanofibers could be obtained from electrospinning with an ordinary single-nozzle electrospinning set-up without the need of a complex spinneret (Angeles, Cheng, & Velankar, 2008; Bazilevsky, Yarin, & Megaridis, 2007; Chen et al., 2011; Hong et al., 2008; Kim et al., 2007; Li and Xia, 2004a, 2004b; Li, Shao, & Liu, 2007; Wei, Kang, Sung, & Mead, 2006). Several works had implemented preparing core–shell structure nanofibers using an ordinary single-nozzle set-up by electrospinning emulsion, in the process of electrospinning, the outer flow was strong enough to stretch the emulsion droplets into the core of the Taylor cone and forming a core–shell jet (Angeles et al., 2008; Bazilevsky et al., 2007; Chen et al., 2011; Hong et al., 2008; Kim et al., 2007; Li et al., 2007; Xu et al., 2006). Nie et al. (Zhang et al., 2009) and Mead et al. (Wei et al., 2006) have obtained core–shell nanofibers by electrospinning a homogeneous solution with an ordinary single-nozzle setup, which was attributed to the kinetic factors due to the rapid solvent evaporation in the process of electrospinning.

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During the process of electrospinning, a high gradient electric potential between the tip of capillary and the collector ever exist. If the high gradient electric potential is fully utilized, controllable two-dimensional (2D) membranes or three-dimensional (3D) microstructures could be obtained, which would be extended in many biomedical and industrial applications (Goldberg, Langer, & Jia, 2007; Kakade et al., 2007; Yang, Zhang, Zhang, & Nie, 2008). In recent years, some researchers have focused on the high gradient electric potential and several methods have been investigated to resolve this issue. For instance, well-aligned nanofibers could be obtained by incorporating assistant electrodes in electrospinning setups or changing the configuration of the collector, which deformed the electric field between the tip of capillary and the collector (Fennessey and Farris, 2004; Li, Wang, & Xia, 2003; Pan, Li, Hu, & Cui, 2006; Sundaray et al., 2004; Wong, Baji, & Leng, 2008; Zussman, Theron, & Yarin, 2003). Besides, Carnell et al. (2008) and Zhang, Yang, Zhang, and Nie (2010) fabricated biaxial orientation pseudowoven mats by incorporating an auxiliary counter electrode, which could convert the electric field to direct the position of the polymer jet. Electrospinning of three-dimensional (3D) microstructures have been achieved by manipulating the electric field to control the jet trajectory. Zhang et al. (Zhang and Chang, 2007; Zhang, Gao, Ji, & Liu, 2008; Zhang, Yang, & Nie, 2008) had fabricated three-dimensional nanofibrous tubes that composed of ultrafine electrospun fibers by manipulating of electric field and electric forces. Previously, we had obtained a bowl-like structure nanofibrous by varying the electric field of the collector (Zhang, Gao, et al., 2008; Zhang, Yang, et al., 2008).

In this work, we report a facile method to fabricate polyelectrolyte based core–shell nanofibers with the assistance of the high gradient electric potential between the tip of capillary and the collector. A homogeneous solution of a polyelectrolyte (hyaluronic acid, sodium alginate and chitosan) and a synthetic polymer (PVA, PVP and PEO) was electrospun with a modified single-nozzle setup. During the electrospinning process, the high gradient electric potential induced the phase separation of the polyelectrolyte based solution, which formed in the glass syringe. As a result, a core–shell jet was ejected from tip of the capillary and core–shell nanofibers were deposited on the collector with the evaporation of solvent.

2. Experimental

2.1. Materials

Hyaluronic acid (HA, $M_w = 8700\,g\,mol^{-1}$) was purchased from Shandong Freda Biopharm Co., Ltd. (Shandong, China). Sodium alginate (SA, 1.28 Pa s) was purchased from Sinopharm Chemical Reagent Co., Ltd. Chitosan (CS, with $M_w = 3000\,g\,mol^{-1}$, about 88% deacetylated) were obtained from Zhejiang Golden-Shell Biochemical Co., Ltd (Yuhuan, Zhejiang, China). PVA ($M_w = 98\,000\,g\,mol^{-1}$, degree of hydrolysis = 88%), PVP (K90, $M_w = 1\,300\,000\,g\,mol^{-1}$) and PEO ($M_w = 900\,000\,g\,mol^{-1}$) were supplied by Acors Organics. The details of the materials are listed in Table 1. All the materials were used without further purification.

2.2. Electrospun solution

HA, CS, SA, PVA, PVP and PEO were all directly dissolved by deionized water with the maximum possible concentration for electrospinning, and then stirred sufficiently until a homogeneous and transparent solution were obtained. All of the electrospinning solutions were blended with fixed solid content ratio at 1:1.

Table 1
The property parameters and maximum possible concentration of polymers.

Component	Density ($mg\,cm^{-3}$)	Hildebrand solubility parameters ($(MPa)^{-1/2}$)	Maximum possible electro spinning concentration (wt%)
HA	1.39	25.07	10
CS	1.44	26.85	10
SA	–[a]	–	2
PVA	1.32	27.82	10
PVP	1.25	21.04	10
PEO	1.22	21.36	8

[a] The detailed information of SA could not be obtained due to the ratio of β-D-mannuronic acid (M) unit and α-L-guluronic acid (G) unit could not be confirmed.

2.3. Electrospinning

A modified electrospinning setup was introduced to produce nanofibers as shown in Fig. 1(a). The solution for electrospinning was transferred into a 5 mL glass syringe with a syringe pump (WSZ-50FZ, Zhejiang University Medical Instrument Co. Ltd) at a constant rate of $0.1\,mL\,h^{-1}$. A high-voltage DC generator (BGG4-21, BMEI CO., Ltd) was used to generate a constant positive high voltage (20.38 kV) between the tip of the needle capillary and collector (18 cm). All the solutions were electrospun at room temperature.

2.4. TEM

The core–shell structure of the nanofibers was characterized by transmission electron microscopy (TEM, S-800, Japan).

2.5. XPS

X-ray photoelectron spectroscopy (XPS) spectra of scaffold were obtained by using a VG ESCALAB MKII X-ray photoelectron spectrometer (VG Scientific Ltd., UK) with Al Kα radiation. Survey spectra were recorded for 0–1350 eV binding energy range.

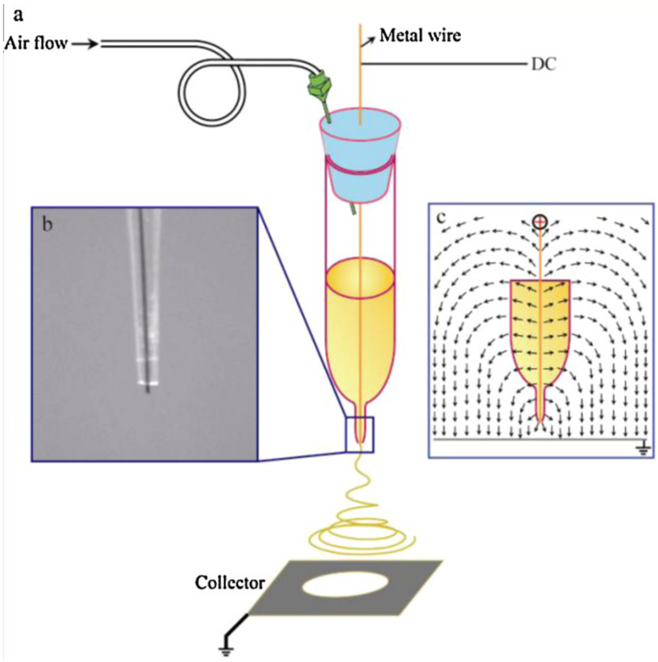

Fig. 1. (a) Schematic representation of the electrospinning setup, (b) the magnified image of the glass syringe needle, and (c) the cross section of the electric field line of the glass syringe.

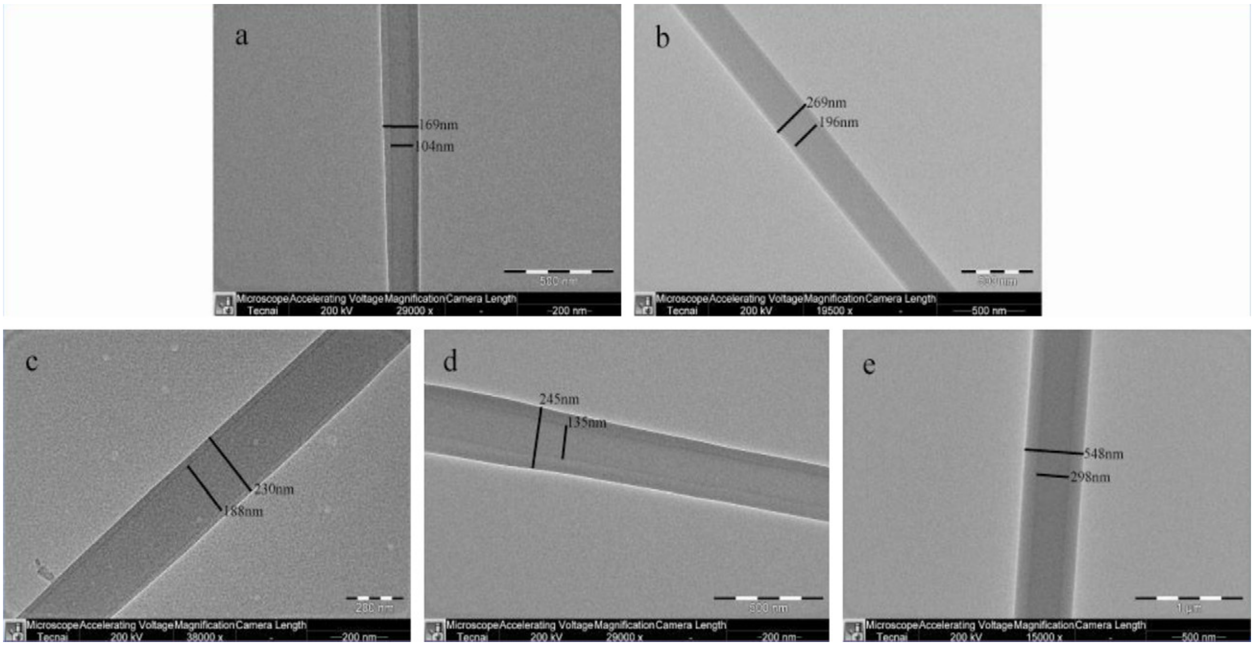

Fig. 2. TEM images of electrospun nanofibers: (a) HA/PVA, (b) CS/PVA, (c) SA/PVA, (d) HA/PVP, and (e) HA/PEO.

2.6. *Electric field experiment*

The electric field experiment was carried out by using a high-voltage DC generator (BGG4-21, BMEI CO., Ltd) to generate a constant positive high voltage (20.38 kV) on the metal wire for 5 min. Then, liquid nitrogen was used to freeze the mixed solution instantly. At last, the sample was transferred into a freeze-drying vessel for at least 48 h to get lyophilized specimen.

3. Results and discussion

Electrospinning of a mixed solution of a polyelectrolyte (HA, CS, or SA) and a synthetic polymer (PVA, PVP, or PEO) revealed an interesting result, the resultant fibers had a core–shell structure. Parts a–c of Fig. 2 display the TEM images of the electrospun core–shell nanofibers from HA/PVA, CS/PVA, and SA/PVA blended solutions, respectively. The element composition of the shell layer was investigated by X-ray photoelectron spectroscopy (XPS) analysis technique in order to corroborate the major composition of the shell. XPS is an analysis method that could get the surface information of the elemental and average chemical composition of a material in 10 nm depth (the thinnest shell of the obtained core–shell nanofibers is more than 20 nm) by measuring the binding energy of electrons associated with atoms (Li et al., 2008). The surface of core–shell nanofiber scaffold showed carbon (binding energy: 285 eV), oxygen (binding energy: 532 eV) and nitrogen (binding energy: 399 eV) (as illustrated in Fig. 3) (Wang et al., 2003). There was nitrogen peak appearing at HA/PVP nanofiber surface, the N_{1s}/O_{1s} ratio for the HA/PVP nanofiber surface was 0.587, which was obviously higher than the N_{1s}/O_{1s} ratio of HA (the calculated value is 0.091), and this confirmed that the composition of the shell was PVP. Nitrogen peak was also observed at CS/PVA nanofiber surface, the N_{1s}/O_{1s} ratio for the CS/PVA nanofiber surface was 0.172, and this demonstrated the shell component was chitosan because PVA has no nitrogen. As to HA/PVA, HA/PEO and SA/PVA nanofibers, there was little or no nitrogen peaks detected, which proved that the polyanion formed the core of the polyanion based core–shell nanofibers. The XPS results revealed that the polyelectrolyte facilitated the formation of core–shell nanofibers.

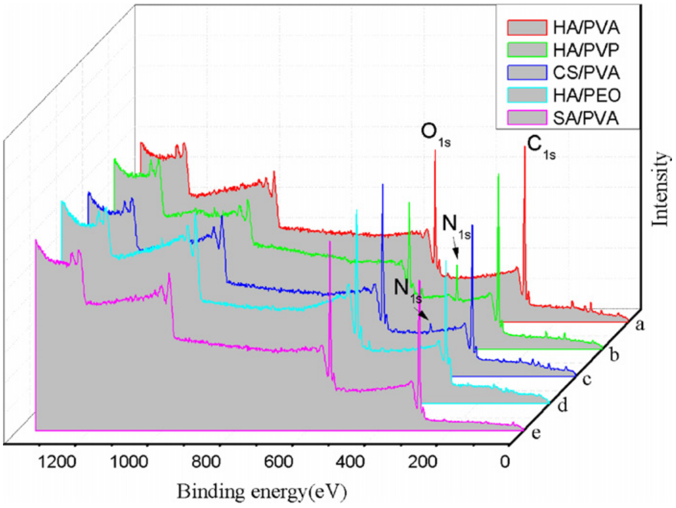

Fig. 3. XPS spectra: (a) HA/PVA, (b) HA/PVP, (c) CS/PVA, (d) HA/PEO, and (e) SA/PVA.

In order to elucidate the process from the mixture to core–shell nanofibers, the effects of electric field on the formation of core–shell fibers had been examined. For the CS/PVA system, CS, a positive charged polymer, was concentrated in the shell of the fibers, and when the CS was replaced by a negative charged polymer such as HA or SA, PVA was concentrated in the shell instead. It was understandable that as polyelectrolyte was dissolved in water, the carboxylic acid group on polyanion would partially ionize or the amino group on polycation would protonize, which would endow polyelectrolyte electrical properties. In our experiment, a highly positive electric potential was employed to form electrospinning jet, and electric force gradient was established between the glass syringe and the collector. The cross section of the electric field line of the glass syringe was shown in Fig. 1(c) (Cui, Li, & Xu, 2011; Li et al., 2003). The force gradient drove the polycation molecules moving in the direction of the electric field line and the polyanion would be opposite (Zhang, Gao, et al., 2008; Zhang, Yang,

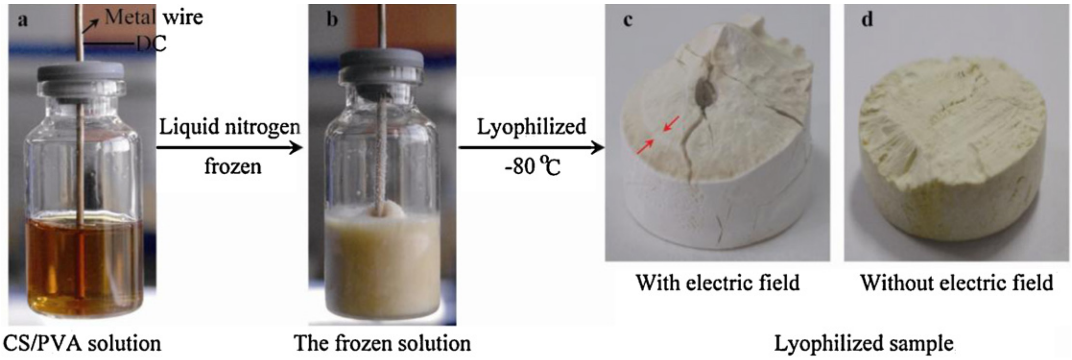

Fig. 4. Schematic illustration for verifying the phase separation of polyelectrolyte based system.

et al., 2008), which facilitated the formation of core–shell structure nanofibers. Thus, the fiber component could be controlled by electric field, and it could be reasonably deduced that the component of core or shell would be transferred when a negative potential was employed.

To further investigate the phase separation process, HA based blending systems were examined, and TEM images were shown in Fig. 2. The core–shell structure of all the HA based blending systems was formed regardless of the solubility parameter difference, which were calculated and shown in Table 1. The solubility parameter difference of the polymers indicated that the thermodynamic factors had a limited influence on the formation of core–shell structures. We considered electric force was the major dominating phase separation driven force, rather than thermodynamic incompatibility in the polyelectrolyte based solution systems. Similar phenomenon was also reported by Mead et al. (Wei et al., 2006), kinetic factors play a much more important role in the development of core–shell fibers. Though the thermodynamic incompatibility was benefit to phase separation, the mobility of polymer molecules played more important roles in the formation of core–shell structure due to the rapid electrospinning process. Besides, the phase separation in the fluid jet occurs when the concentration of solution was higher than a critical concentration (C_{ps}) that the decreased solvation effect could not prevent blending polymer from phase separating, and the phase separation process was end as the mobility of polymer prohibited (the concentration was defined as C_{pf}). Accordingly, the phase separation window ($C_{ps} \sim C_{pf}$) in electrospinning process was narrow, and the phase separation time was very short due to the rapid evaporation of the solvent. Thus, the rapid mobility of polymers became the key parameter on the formation of core–shell structures. For the polyelectrolyte based blending systems, the electric force enhanced the mobility of polyelectrolyte molecules. Furthermore, electric field enlarged the phase separation window of the electrospinning process for polyelectrolyte based blending systems. In electric field, the polyelectrolyte moved with the electric field line despite of the large fraction of solvent in the solution. In this case, the phase separation occurs as soon as high electric field was applied to the electrode, and the phase separation could be stopped until the jet solidified. The phase separation time elongated from several milliseconds to a few minutes.

For further investigation of the influence of electric field on the phase separation process, an electric field experiment was carried out. The schematic of the process was shown in Fig. 4. From the cross-section of the specimen, there was a distinct dividing line as shown by the red arrows in Fig. 4(c). The color of the outer layer of the specimen was much darker than the inner layer, which was contributed by the movement of CS to the outer layer. The results proved that electric field was the main cause on phase separation, which occurred in polyelectrolyte based blending solution during electrospinning process and the phase separation time was significantly elongated simultaneously.

4. Conclusion

Polyelectrolyte based core–shell nanofibers could be prepared by electrospinning a homogeneous solution of a polyelectrolyte (hyaluronic acid, sodium alginate and chitosan) and a synthetic polymer (PVA, PVP and PEO) with the assistance of electric field. In the process, polycation formed the shell layer, while polyanion formed the core. Electric field was the major effect of the phase separation. In the process, electric field enlarged the phase separation window ($C_{ps} \sim C_{pf}$), which elongated the phase separation time from several milliseconds to a few minutes, and core–shell structure nanofibers were obtained. The polyelectrolyte based core–shell nanofibers membrane would show a potential application in biomedical field.

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