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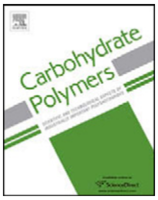

Electrospinning of chitosan nanofibers: The favorable effect of metal ions

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ABSTRACT

This study is aimed to assess the doping effects of monovalent, bivalent, and trivalent metal ions on the morphological appearance of the electrospun chitosan/poly(ethylene oxide) (PEO) blend nanofibers. Scanning electron micrographs confirmed that the presence of 0.4–1.6 wt% NaCl (or KCl) in the blend solutions produced nanofibers, accompanying re-crystallization of inorganic salts, while addition of appropriate amounts of $CaCl_2$ or $FeCl_3$ (~0.8 wt%) resulted in beneficial effect on defect-free nanofibers. The Fourier transform infrared spectra and rheological analysis results implied that the addition of metal ions were favorable for decreasing the viscosity (45–60%) and hydrogen bonds of the blends. Moreover, the fabrication of metal-ion-modulated chitosan/PEO nanofibers would lend experience to processing binary, ternary or multinary biologically active trace elements-codoped nanofibers via electrospinning. This general electrospinning strategy, which involves doping of metal ions, may be versatile to modulate the fibrous structure and functionality of polymers.

1. Introduction

The use of electrohydrodynamics to produce organic polymer fibers is well documented (Li & Xia, 2004). In brief, solutions or melts are pumped through a nozzle at very low flow rates (normally 0.1–1.0 mL h^{-1}), and the solvent in the jet stream rapidly evaporates during fiber formation. Electrospinning is developing fastly because of its ability to produce fibrous mats with high surface area that can be used in biomedical and other scientific areas (Agarwal, Wendorff, & Greiner, 2008; Jayakumar, Prabaharan, Nair, & Tamura, 2010). In order to generate electrospun fibers successfully on a typical laboratory electrospinning setup, specific solution properties (e.g. viscosity, electrical conductivity), process parameters (e.g. electrical field strength, fluid flow rate), and environmental humidity should be considered (Agarwal et al., 2008; Liu et al., 2010; Theron, Zussman, & Yarin, 2004).

Chitosan is a natural copolymer of glucosamine and N-acetylglucosamine and it has an amine functional group which is strongly reactive with inorganic anions (Varma, Deshpande, & Kennedy, 2004). Chitosan is hypoallergenic and is widely studied owing to its excellent wound healing acceleration and natural antibacterial properties (Muzzarelli, 2009; Mitani, Nakalima, Sungkano, & Ishii, 1995; Torres-Giner, Ocio, & Lagaron, 2008). Electrospinning of chitosan is a promising process to produce fibrous mats with fiber diameter of ~100 nm. However, electrospinning of pure chitosan from its aqueous solution remains to be a problem due to its high viscosity and strong hydrogen bonds (Homa, Seyed, Hosseini, & Masoumeh, 2009; Geng, Kwon, & Jang, 2005). Thus, spinnability of chitosan deserves a special attention, since there is a need for versatile pathway to improve fibrous structure without involving labor-intensive procedure.

It has been reported that individual chitosan fibers could be produced with the utilization of non-aqueous solvents. For instance, the pure chitosan has been electrospun from harmful solvents such as trifluroacetic acid (Ohkawa, Cha, Kim, Nishida, & Yamamoto, 2004) and hexafluoro propanol (Min et al., 2004). Meanwhile, chitosan blends with other polymers, such as polyvinyl alcohol (PVA) (Son, Yeom, Song, Lee, & Hwang, 2009), polyacrylamide (Desai & Kit, 2008), polyethylene oxide (PEO) (Klossner, Queen, Coughlin, & Krause, 2008), and zein (Torres-Giner, Ocio, & Lagaron, 2009) have been used to electrospin composite fibers. On the other hand, there are a few reports in literature on the use of inorganic ions or nanoparticles as doping agents for producing electrospun fibers (Ji, Medford, & Zhang, 2009; Saquing, Manasco, & Khan, 2007). Zhu et al. reported that calcium ions deteriorated spinnability of PVA solutions due to the intermolecular crosslinking occurred between PVA chain and metal ions that resulted in the abnormal surface tension (Zhu, Gao, Xu, & Xu, 2007). One of the major applications of chitosan and its many derivatives are based on its ability to chelate metal ions (Muzzarelli, 1996, 1973). However, very little work is

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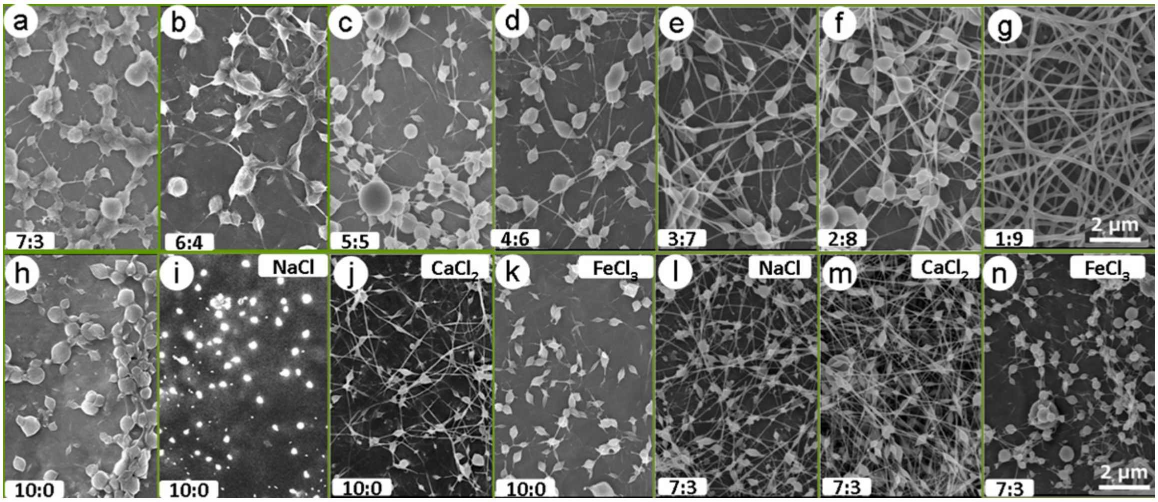


Fig. 1. SEM images of electrospun products with different chitosan/PEO ratio. (a–g) The products from the chitosan/PEO blend solutions, (h) the products from the chitosan solution, (i–k) the products from the chitosan solutions containing 0.4 wt% inorganic salts, (l–n) the products from the chitosan/PEO blend solutions containing 0.4 wt% inorganic salts. Inset data is the chitosan/PEO weight ratio in the solutions.

focusing on the effect of metal ions on morphology and integrity of electrospun chitosan products.

In this study, a variety of metal ion-modulated chitosan/PEO electrospun nanofibers were produced and investigated. PEO is chosen as a counterpart because it is a hydrophilic, protein resistant polymer which allows a slowed clearance of the carried protein from blood (Harbers et al., 2007). Thus the chloride salts of monovalent (Na^+, K^+), bivalent (Ca^{2+}, Sr^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+}), and

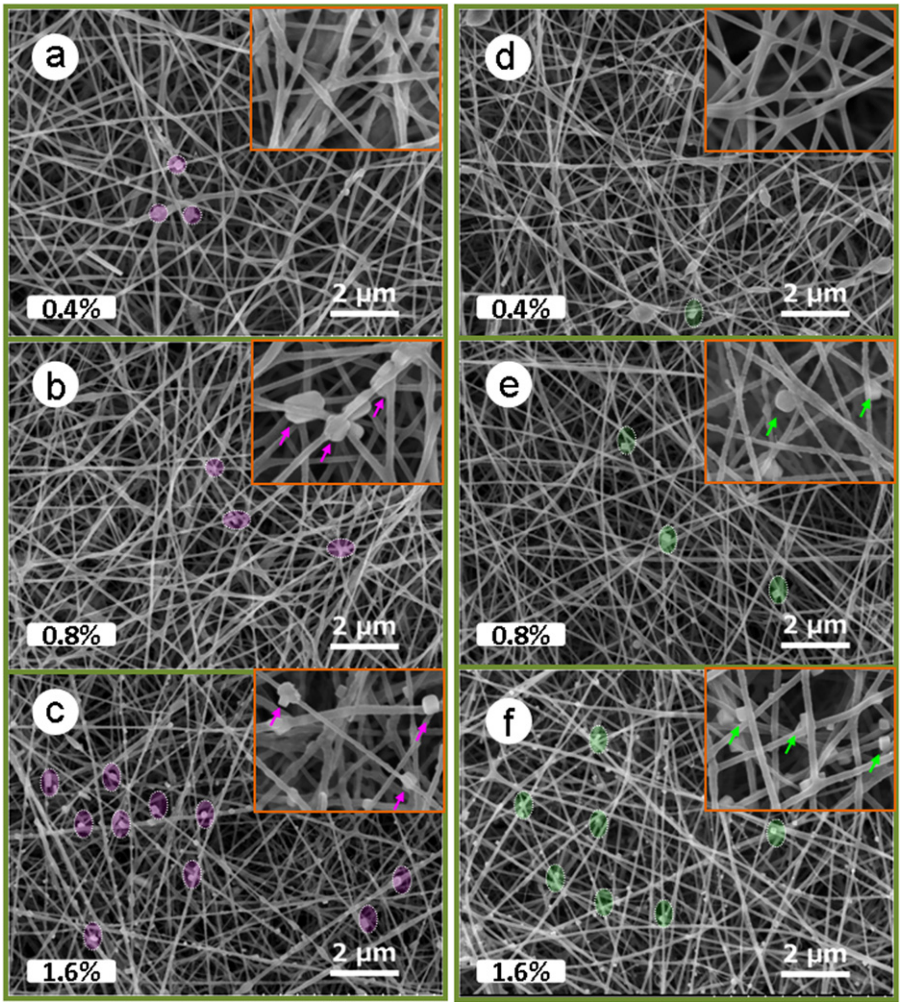


Fig. 2. SEM images of electrospun nanofibers from the chitosan/PEO blend solution (chitosan/PEO = 3:7) in the presence of 0.4–1.6 wt% NaCl (a–c) and KCl (d–f), respectively. The circled and arrowed beads were NaCl and KCl nanocrystals, respectively.

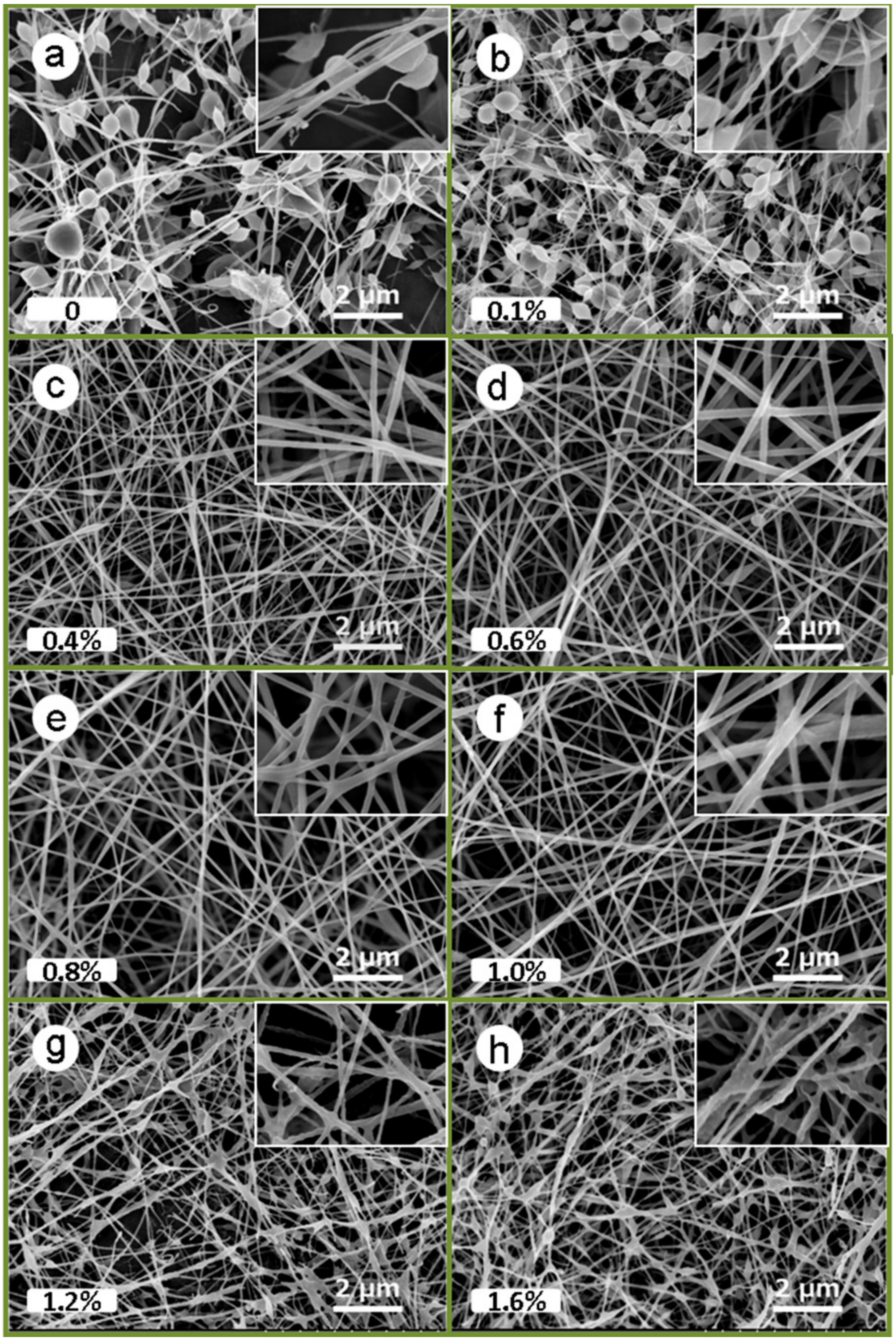


Fig. 3. SEM (magnified) images of nanofibers from the chitosan/PEO blend solution (chitosan/PEO = 3:7) in the absence (a) and presence (b–f) of 0.1–1.2 wt% $CaCl_2$, respectively.

trivalent (Fe^{3+}) on the spinnability of chitosan/PEO blends was studied.

2. Materials and experiment

2.1. Chemicals and solution preparation

Chitosan ($M_W = 50$ kDa) with a degree of deacetylation of 90% was purchased from Haidebei Marine Bioengineering Inc., China. PEO ($M_W = 700$ kDa) was obtained from Sinopharm Chemical Reagent Inc., China. The reagent grade NaCl, KCl, $CaCl_2$, $MgCl_2$, $SrCl_2$, $ZnCl_2$, and $FeCl_3$ (BBI, Canada) were used as received. Firstly, the inorganic salt solutions (16 wt%) of monovalent (Na^+, K^+), bivalent (Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}), and trivalent (Fe^{3+}) metal ions were prepared in deionized water and then filtered through a 0.22-μm pore membrane, respectively. The chitosan (3.0 wt%, in 0.5 wt% acetic acid) and PEO (5.0 wt%) solutions were also prepared, respectively. Then the chitosan/PEO blend solutions with different chitosan/PEO ratio and inorganic salt concentrations were prepared by mixing appropriate amounts of the solutions above.

2.2. Electrospinning of metal ion-free chitosan/PEO solutions

A series of chitosan/PEO composites were prepared with a variety of chitosan/PEO ratio. In a typical procedure, 5 mL blend solution with chitosan/PEO = 3:7 (*w*/*w*) was loaded into the syringe equipped with a metal needle, and the needle was connected to a high-voltage power supply (ES30-20W, Dongwen High Voltage

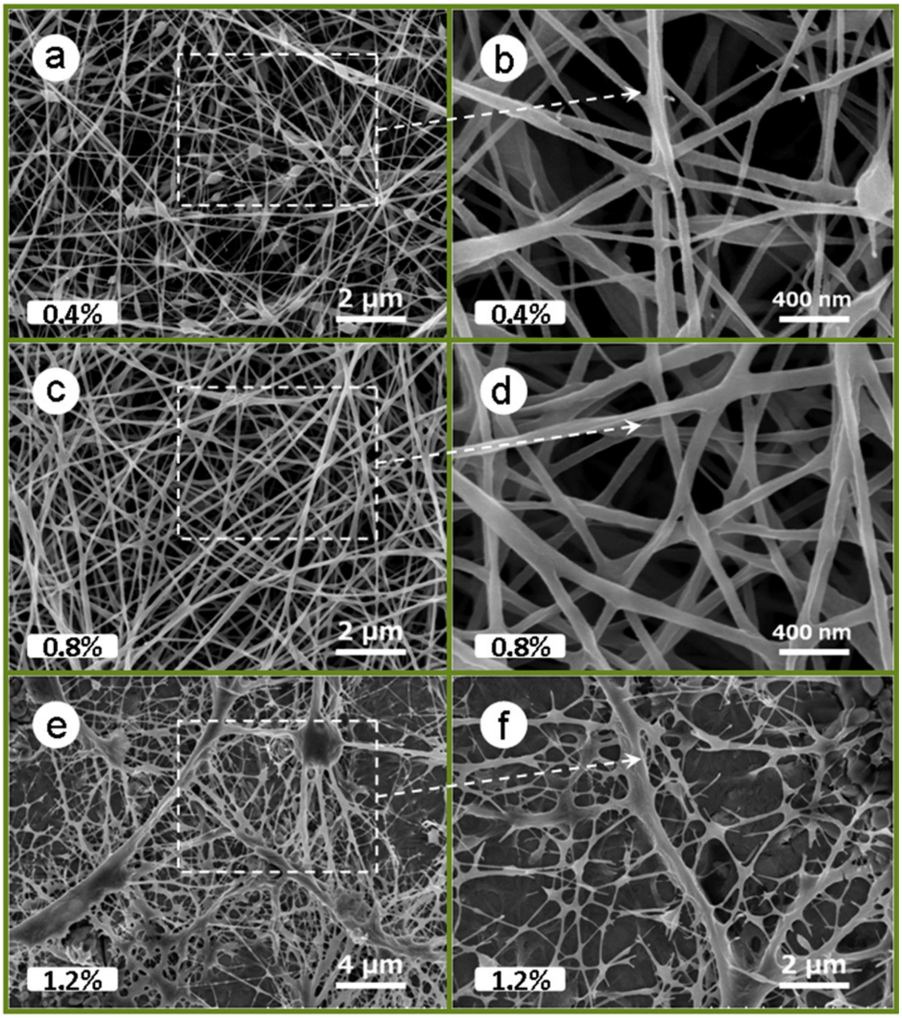


Fig. 4. SEM images of nanofibers from the chitosan/PEO blend solution (chitosan/PEO = 3:7) in the presence of 0.4%–1.2 wt% $FeCl_3$, respectively.

Inc., China). The solution was continuously supplied using a syringe pump at a rate of 0.2 mL h^{-1}. The voltage was 12 kV and collection distance was 8 cm. A typical collecting time was 5 min. The grounded aluminum foil was used as collector. The spinning process was conducted in a lab-made glove box, in which the relative humidity was controlled at the level of ∼20%.

2.3. Electrospinning of metal ion-rich chitosan/PEO solutions

In a typical procedure, 5 mL of blend solution with chitosan/PEO = 3:7 and 0.4 wt% NaCl was loaded into the syringe. The solution was continuously supplied using a syringe pump at a rate of 0.2 mL h^{-1}, while the other conditions remained constant. Similarly, fibers were prepared using solutions with KCl by the same method.

To investigate the effect of bivalent metal ions on chitosan/PEO fibers, the fibers were prepared with $CaCl_2$ concentration of 0.4–1.6 wt%, with chitosan/PEO ratio of 3:7, while the other conditions remained constant. Similarly, the effect of Fe^{3+} ions on fibers was tested for the chitosan/PEO blend solutions with $FeCl_3$ concentration of 0.4–1.2 wt%, while the other conditions remained constant.

In addition, an array of biologically active trace element metal (magnesium, strontium, zinc, and iron) chloride was also added into the chitosan/PEO blend solutions and electrospun under the same conditions. The polymer solutions containing the unitary Mg^{2+}, Sr^{2+}, Zn^{2+} or Fe^{2+} ions with 0.8 wt% salt concentration were firstly electrospun, respectively. Then the binary (Mg^{2+}–Sr^{2+}), ternary (Mg^{2+}–Sr^{2+}–Zn^{2+}, Mg^{2+}–Sr^{2+}–Fe^{2+}), and quaternary (Mg^{2+}–Sr^{2+}–Zn^{2+}–Fe^{2+}) combination of trace elements with equal salt concentration (0.2 wt%) were added into the chitosan/PEO blend solutions and electrospun, respectively.

2.4. Characterization

The electrospun products were determined by Fourier transform infrared spectroscopy (FTIR; Nicolet). The morphology of products was observed using scanning electron microscopy (SEM; HITACHI, S4800) and transmission electron microscopy (TEM; JEOL, JEM-1230). The thermal analysis of the fiber mats, performed using a thermogravimetric and differential thermalgravi-metric analysis (TG-DTA; Perkin Elmer, USA), was carried out with heating rate of 10 °C min^{-1} in air. Moreover, the as-dried samples were treated at 600 °C for 1 h in an electric furnace and followed by SEM observation. Rheology measurement was performed on a strain-controlled rheometer ARES with coquette geometry (TA Instruments, USA) at 25 °C. Frequency sweeps were carried out for angular frequencies ω = 0.1–100 rad s^{-1} at a strain amplitude of 1.0%. The steady state was used to determine the viscosity, recorded as a function of shear rate.

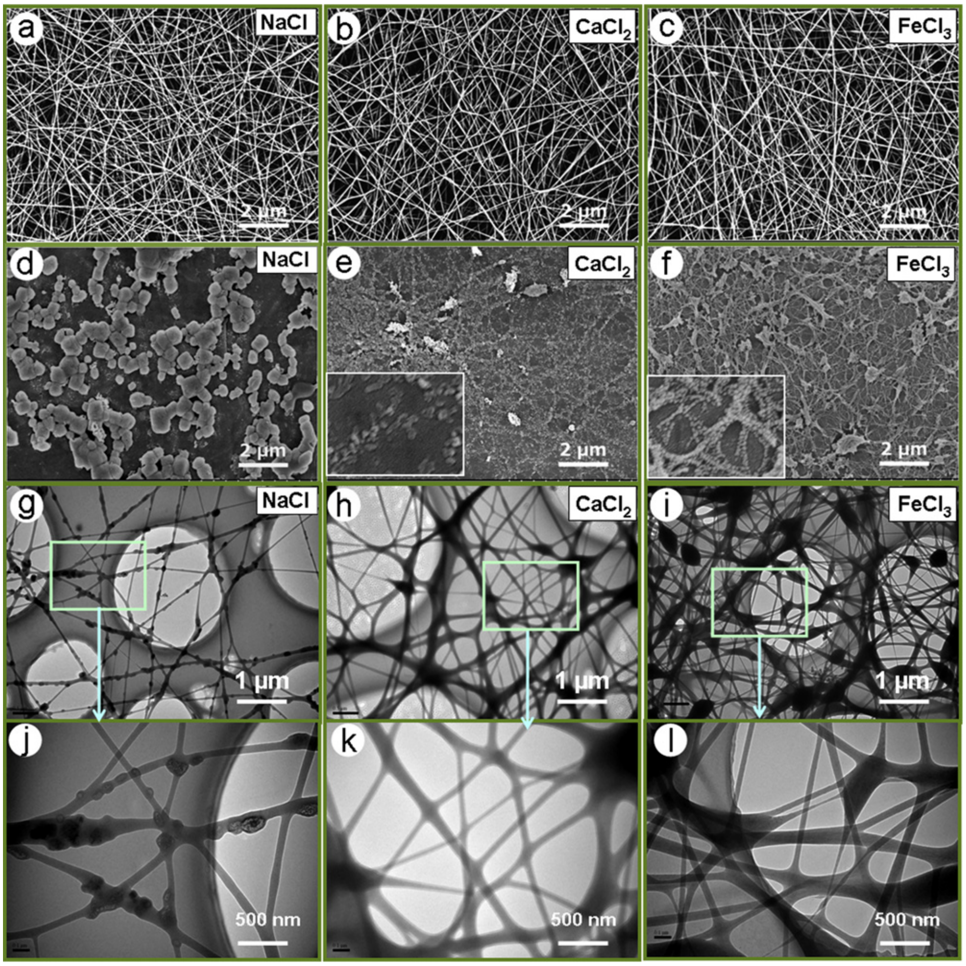


Fig. 5. SEM (a–f) and TEM (g–l) images of electrospun chitosan/PEO nanocomposites from the chitosan/PEO blend solutions (chitosan/PEO = 3:7) containing 0.8 wt% inorganic salts before (a–c) and after (d–f) thermal treatment at 600 °C.

3. Results and discussion

3.1. SEM observation

Chitosan, as a natural polyelectrolyte, can dissolve well in dilute acid in a wide range of concentrations. Electrospinning of various chitosan aqueous solutions with different PEO and/or metal ion doping was tried firstly. It was observed that the droplets were generated when limited amounts of PEO were doped in the chitosan solutions (Fig. 1a and b). As a rule, along with the increase of relative amount of PEO, the electrospun products became continuous, and short fibers or “bead-on-the-string” morphology could be generated (Fig. 1c–f), but smooth fibers were not found until the chitosan/PEO ratio increased to 1:9 (Fig. 1g). As for the metal ion-doped chitosan and chitosan/PEO electrospinning (Fig. 1i–n), the monovalent (Na^+), bivalent (Ca^{2+}) and trivalent (Fe^{3+}) metal chloride could be favorable for improving the fibrous morphology of chitosan/PEO blends at the chitosan/PEO ratio of 7:3. These results imply that PEO and metal ions have a synergistic effect on the spinnability of chitosan.

To determine the influence of monovalent metal ions (i.e., Na^+ or K^+) on the spinnability of CHI/PEO blend solution, the experiments were carried out at the chitosan/PEO ratio of 3:7, which is the optional condition of poor spinnability for the chitosan/PEO blend. Electrospinning of solutions in the presence of monovalent Na^+ or K^+ ions resulted in fibers comprising chitosan and PEO (Fig. 2). It was observed that with increasing the concentration of metal ions, more and more nanocrystals re-crystallized with chloridion (Cl^-) ions in the nanofibers when water evaporated completely.

To determine the effect of bivalent metal ion on the formation of nanofibers, the chitosan/PEO blends were electrospun in the presence of different amounts of $CaCl_2$ (0–1.2 wt%). The bead-rich fibers could be obtained if no $CaCl_2$ was added (Fig. 3a). By addition of 0.1 wt% $CaCl_2$, bead-defects formed in the fibers (Fig. 3b), suggesting that the limited amount of $CaCl_2$ do not give rise to beadless fibers. With the increase of $CaCl_2$ amounts to 0.4–1.0 wt% in aqueous solutions uniform fibers with average diameter of ~200 nm (Fig. 3c–e) could be observed. However, when $CaCl_2$ was added in the same system, the productions showed bad trend of getting thicker fibers (Fig. 3f). This may be due to excessive elongation forces with the concomitant tremendous increase in the solution conductivity (Saquing et al., 2007).

By addition of appropriate amounts of $FeCl_3$, the formation of fibers was also promoted (Fig. 4a–d). Usually, the uniform iron-based fibers could be generated via electrospinning the Fe salt-containing polymer solutions (Wu, Zhang, & Liu, 2007). Thus it is reasonable to postulate that Fe^{3+} ions may be favorable for chitosan/PEO fiber formation. However, the integrity of fibrous structure is also negatively influenced by the excessive concentration of Fe^{3+} ions (branched fibers as shown in Fig. 4e and f).

The morphology of nanocomposite mats before and after calcination treatment was observed by SEM (Fig. 5a–f). It can be seen that the defect-free fibers were generated from the blend solutions containing 0.8 wt% inorganic salts, whereas the calcined

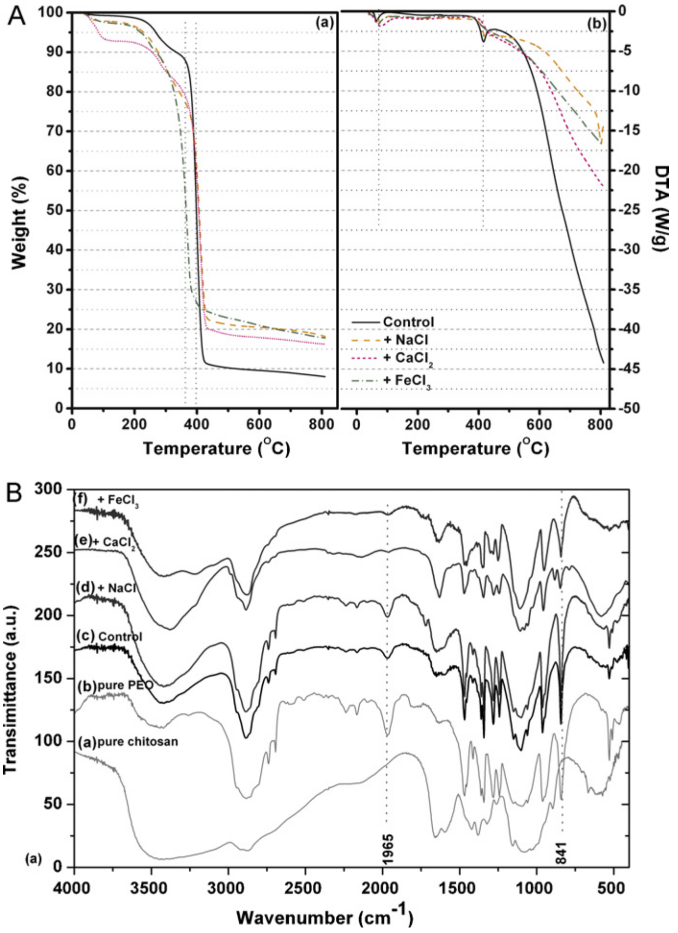
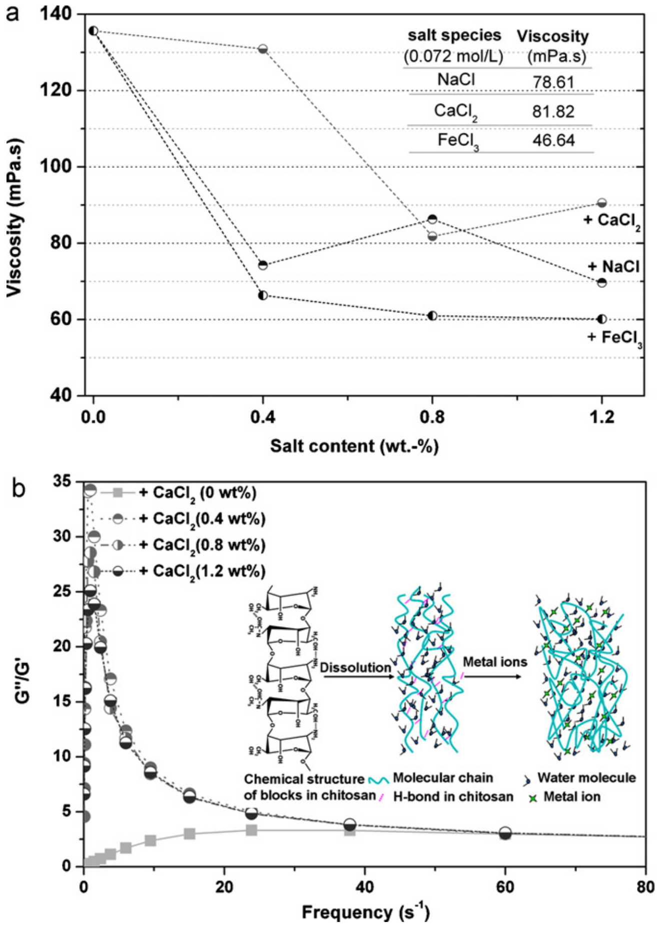


Fig. 6. TG-DTA profile (A) and FTIR spectra (B) of the inorganic salt (0.8 wt%)-mediated chitosan/PEO nanocomposite fibers from the chitosan/PEO blend solution (chitosan/PEO = 3:7). Data on the chitosan/PEO products without metal ions is shown as control.



salt species (0.072 mol/L)	Viscosity (mPa.s)
NaCl	78.61
CaCl$_2$	81.82
FeCl$_3$	46.64

Fig. 7. Viscosity of the chitosan/PEO blend solutions in the absence and presence of inorganic salts (a) and plots of G″/G′ ratio versus frequency for the as-prepared chitosan/PEO in the presence of different amount of CaCl$_2$ (b). Inset in (a) shows the viscosities for the systems with equal molar of metal ion charges.

products revealed only inorganic particles on the foil by the monovalent metal ion modulation, which is characteristic of the typical NaCl crystals (Fig. 5d). In the bivalent and trivalent metal ion-incorporated mats, the fibrous structures were observed (Fig. 5e and f). Furthermore, the TEM images also provided the different fibrous structures between NaCl-doped fibers and CaCl$_2$- and FeCl$_3$-doped fibers, as seen at low magnification (Fig. 5g–i). The high-magnification images clearly revealed the existence of only NaCl crystals in the fibers (Fig. 5j–l). These results confirm that the alkaline metal ions recrystallize preferentially with chloridions when water and acetic acid evaporate, but calcium and iron ions distribute in the fibers homogeneously possibly due to the intermolecular and intramolecular crosslinking occurred between the protonated chitosan and metal ions.

3.2. TG-DTA and FTIR analysis

The inorganic salt (0.8 wt%)-modulated nanofibers were further analyzed by TG-DTA (Fig. 6A). It can be seen from Fig. 6A(a) that the difference of decomposition temperatures for the nanofibers containing monovalent and bivalent metal ions was negligible, similar to the control (∼398 °C). The iron-doped nanofibers exhibited lower decomposition temperature (∼355 °C). It would mean that the composite nanofibers can be treated by autoclaving prior to biomedical application. On the other hand, with regard to the weight loss (over 90%) for the control, the samples containing metal ions had less weight loss (∼80%) at 600 °C due to the inorganic residues. As for DTA curves, the samples exhibited two small endothermic peaks, between 80 and 400 °C (Fig. 6A(b)). The first one, at about 90 °C, should be ascribed to the removal of adsorbed (non-lattice) water, whereas the second one corresponded to the organic component decomposition in the composites, which occurred at about 390 °C.

The FTIR spectra of chitosan/PEO nanofibers proved the existence of chitosan and PEO (Fig. 6B). The FTIR spectrum of chitosan showed bands at 1154 and 893 cm^{-1} identifying its saccharide groups. Other bands at 1600, 1651 and 3425 cm^{-1} depicted N–H bending of the primary amino groups, the carbonyl stretching of the amide bands, and the N–H stretching of the primary amino groups, respectively. It was clearly shown that the decrease of bands at ∼1965 and 841 cm^{-1} for the products containing CaCl$_2$ and FeCl$_3$ implied these bivalent and trivalent ions interacted strongly with the polymers and weakened the hydrogen bond of polymers. It is possible to partly explain the influence of metal ions on the spinnability of chitosan/PEO blends.

3.3. Rheological analysis

Rheological measurements were carried out to understand the effect of metal ions on the conformation and hydrodynamic behavior of chitosan/PEO solutions. Fig. 7a shows the relationship between viscosity of solutions and concentration of inorganic salts. While the original viscosity of chitosan/PEO solution was high (135.6 mPa s), increasing concentration of inorganic salts could lead

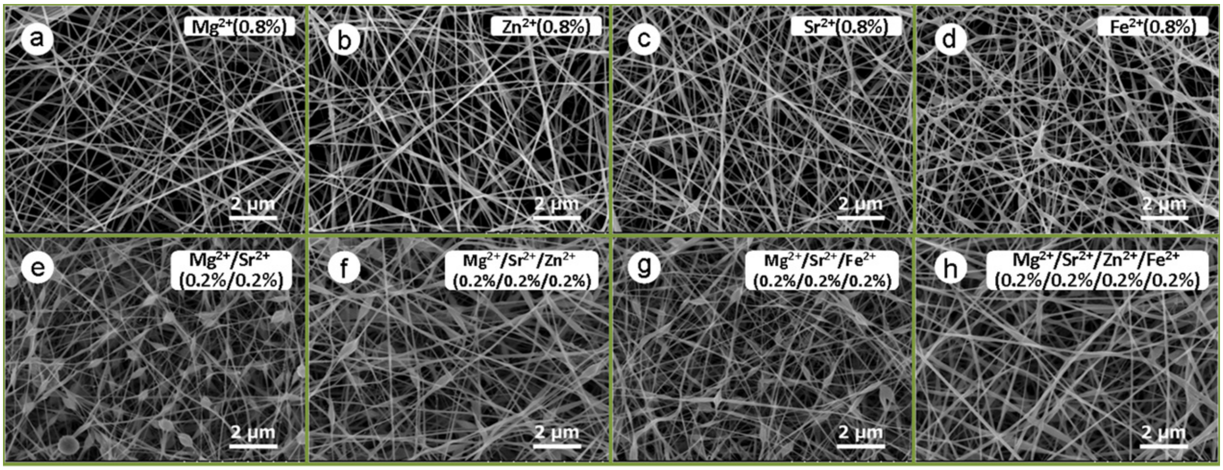


Fig. 8. SEM images of electrospun unitary, binary, ternary and quaternary trace element-doped nanofibers fabricated from the chitosan/PEO blend solution (chitosan/PEO = 3:7) in the presence of Mg^{2+}, Zn^{2+}, Sr^{2+}, and/or Fe^{2+}, respectively.

to decrease in viscosity, and particularly a significant change could be observed at salt concentration over 0.8% (<90 mPa s). This possibly resulted from the decreasing bonding strength between the side chains of chitosan with increasing metal ion concentration in the solutions, which promote its molecular movement. In addition, both G'' and G' of the $CaCl_2$-added chitosan/PEO blend solutions were measured with the increase of $CaCl_2$ concentration. It can be seen from Fig. 7b that the G''/G' ratio firstly increased at low frequency and then decreased at high frequency ($>2\,s^{-1}$), but G''/G' ratio were all >1 ($G'' > G'$), which indicated a viscoelastic system. These results reflect convincingly the fact that the combined contribution of enhanced chain entanglement and increased conductivity (via decreasing viscosity and destroying hydrogen bonds) by metal ions may be the key reasons for the improved spinnability (see inset in Fig. 7b).

3.4. SEM observation for the trace elements-doped nanofibers

To demonstrate the versatility of the inorganic metal ion on the spinnability of chitosan/PEO blend solutions, we extended the experimental study to other biologically active trace elements. With the same method, the spinnability of chitosan/PEO blend solutions was improved by trace element-monodoping, similar to the case for divalent calcium ions (0.8 wt%), as evidenced in Fig. 8a–d. These pictures indicated that the trace element metal ions did not recrystallize during water rapid evaporation. Moreover, the impact of *binary*, *ternary*, and *quaternary* trace elements co-doping on the spinnability of chitosan/PEO under the analogous blend solution conditions was also studied to further validate the mechanism (0.4–0.8 wt% in total). As expected, upon addition of multiple trace elements in the blend solutions, fibrous structures improved, and their diameters tended to be nanoscale dimension with increasing ionic concentration from 0.4 to 0.8 wt% in total (Fig. 8e–h). These fibrous nanostructures with improved bioactivity by multiple trace elements doping may find numerous potential applications such as wound dressing, guided bone regeneration membrane, and so on.

4. Conclusion

In this study, the favorable effect of inorganic salts on the spinnability of chitosan/PEO blends has been approved in the extent of reaction/product yield. The calcium and iron ions demonstrated a similar behavior on reducing fiber diameter and the number of beads in fibers, whereas NaCl or KCl nanocrystals occurred in the fibers containing the alkali metal ions. FTIR and rheological measurements indicated that metal ions could disrupt inter- and intra-molecular hydrogen bonds of chitosan and decrease viscosity of the solutions so that chitosan chain entanglements may be enhanced significantly. It is expected to design and develop nonwoven membranes for protein resistance or affinity to biologically active trace elements. This study also provides a fundamental understanding and possible solution to electrospin naturally occurring biopolymers in complicated aqueous solutions.

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References

Agarwal, S., Wendorff, J. H., & Greiner, A. (2008). Use of electrospinning technique for biomedical applications. *Polymer*, *49*, 5603–5621.

Desai, K., & Kit, K. (2008). Effect of spinning temperature and blend ratios on electrospun chitosan/poly(acrylamide) blends fibers. *Polymer*, *49*, 4046–4050.

Geng, X. Y., Kwon, O. H., & Jang, J. H. (2005). Electrospinning of chitosan dissolved in concentrated acetic acid solution. *Biomaterials*, *26*, 5427–5432.

Harbers, G. M., Emoto, K., Greef, C., Metzger, S. W., Woodward, H. N., Mascali, J. J., et al. (2007). A functionalized poly(ethylene glycol)-based bioassay surface chemistry that facilitates bio-immobilization and inhibits non-specific protein, bacterial, and mammalian cell adhesion. *Chemistry of Materials*, *19*, 4405–4414.

Homa, H., Seyed, R., Hosseini, A., & Masoumeh, V. (2009). Electrospinning of chitosan nanofibers: Processing optimization. *Carbohydrate Polymers*, *28*, 142–150.

Jayakumar, R., Prabaharan, M., Nair, S. V., & Tamura, H. (2010). Novel chitin and chitosan nanofibers in biomedical applications. *Biotechnology Advances*, *28*, 142–150.

Ji, L., Medford, A. J., & Zhang, X. (2009). Electrospun polyacrylonitrile/zinc chloride composite nanofibers and their response to hydrogen sulfide. *Polymer*, *50*, 605–612.

Klossner, R. R., Queen, H. A., Coughlin, A. J., & Krause, W. E. (2008). Correlation of chitosan's reological properties and its ability to electrospun. *Biomacromolecules*, *9*, 2947–2953.

Li, D., & Xia, Y. (2004). Electrospinning of nanofibers: Reinventing the wheel? *Advanced Materials*, *16*, 1151–1169.

Liu, Y., Ma, G., Fang, D., Xu, J., Zhang, H., & Nie, J. (2010). Effects of solution properties and electric field on the electrospinning of hyaluronic acid. *Carbohydrate Polymers*, 061, doi:10.1016/carbopol.2010.08.

Min, B. M., Lee, S. W., Lim, J. N., You, Y., Lee, T. S., & Kang, P. H. (2004). Chitin and chitosan nanofibers: Electrospinning of chitin and deacetylation of chitin nanofibers. *Polymer*, *45*, 7137–7142.

Mitani, T., Nakalima, C., Sungkano, I. E., & Ishii, H. (1995). Effects of ionic strength on the adsorption of heavy metals by swollen chitosan beads. *Journal of Environmental Science and Health Part A*, *30*, 669–674.

Muzzarelli, R. A. A. (2009). Chitins and chitosans for the repair of wounded skin, nerve, cartilage and bone. *Carbohydrate Polymers*, *76*, 167–182.

Muzzarelli, R. A. A. (1996). Chitin: Metal ion chelation and enzyme immobilization. In J. C. Salamone (Ed.), *The polymeric materials encyclopedia* (pp. 295–300). Boca Raton, FL, USA: CRC Press, Inc.

Muzzarelli, R. A. A. (1973). *Natural chelating polymers*. Oxford: Pergamon Press.

Ohkawa, K., Cha, D. I., Kim, H., Nishida, A., & Yamamoto, H. (2004). Electrospinning of chitosan. *Macromolecular Rapid Communications*, *25*, 1600–1605.

Saquing, C. D., Manasco, J. L., & Khan, S. A. (2007). Electrospun nanoparticle-nanofiber composites via a one-step synthesis. *Small*, *5*, 944–951.

Son, B., Yeom, B.-Y., Song, S. H., Lee, C.-S., & Hwang, T. S. (2009). Antibacterial electrospun chitosan/poly(vinyl alcohol) nanofibers containing silver nitrate and titanium dioixed. *Journal of Applied Polymer Science*, *111*, 2892–2899.

Theron, S. A., Zussman, E., & Yarin, A. L. (2004). Experimental investigation of the governing parameters in the electrospinning of polymer solutions. *Polymer*, *45*, 2017–2030.

Torres-Giner, S., Ocio, M. J., & Lagaron, J. M. (2008). Development of active antimicrobial fiber based chitosan polysaccharide nanostructures using electrospinning. *Engineering in Life Sciences*, *8*, 303–314.

Torres-Giner, S., Ocio, M. J., & Lagaron, J. M. (2009). Novel antimicrobial ultrathin structures of zein/chitosan blends obtained by electrospinning. *Carbohydrate Polymers*, *77*, 261–266.

Varma, A. J., Deshpande, S. V., & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivatives: A review. *Carbohydrate Polymers*, *55*, 77–93.

Wu, H., Zhang, R., & Liu, X. (2007). Electrospinning of Fe, Co, and Ni nanofibers: synthesis, assembly, and magnetic properties. *Chemistry of Materials*, *19*, 3506–3511.

Zhu, X., Gao, Q., Xu, D., & Xu, Y. (2007). Improvement of the electrospinnability of polyvinyl alcohol via dialysis and complexation pretreatment. *Journal of Polymer Research*, *14*, 277–282.