Fabrication and formation mechanism of closed-loop fibers by electrospinning with a tip collector*

Xu Yan(闫旭)[1,†], Miao Yu(于淼)[1,2,†], Wen-Peng Han(韩文鹏)[1], Ming-Hao You(犹明浩)[1], Jun-Cheng Zhang(张君诚)[1], Rui-Hua Dong(董瑞华)[1], Hong-Di Zhang(张红娣)[1], and Yun-Ze Long(龙云泽)[1,3,‡]

[1] *Collaborative Innovation Center for Low-Dimensional Nanomaterials & Optoelectronic Devices, College of Physics, Qingdao University, Qingdao* 266071, *China*

[2] *Department of Mechanical Engineering, Columbia University, New York* 10027, *USA*

[3] *Collaborative Innovation Center for Marine Biomass Fibers, Materials and Textiles of Shandong Province, State Key Laboratory Cultivation Base of New Fiber Materials and Modern Textile, Qingdao University, Qingdao* 266071, *China*

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Electrospun nanofibers with designed or controlled structures have drawn much attention. In this study, we report an interesting new closed-loop structure in individual cerium nitrate/polyvinyl alcohol ($Ce(NO_3)_3$/PVA) and NaCl/PVA fibers, which are fabricated by electrospinning with a nail collector. The electrospinning parameters such as voltage and $Ce(NO_3)_3$ (or NaCl) concentration are examined for the formation of the closed-loop structure. The results suggest that the increase of the spinning voltage or addition of $Ce(NO_3)_3$ (or NaCl) is favorable for the formation of the closed-loop structure, and the increase of loop numbers and the decrease of loop size. Further analyses indicate that the formation mechanism of the closed-loop fibers can be predominantly attributed to the Coulomb repulsion in the charged jets.

Keywords: electrospinning, nail collector, closed-loop fiber, Coulomb repulsion

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1. Introduction

Over the past few decades, electrospinning, as a simple, versatile, and useful technique for fabricating nanofibers, has attracted much attention.[1–5] By electrospinning, a great variety of polymers have been electrospun into micro- and nanofibers and the as-spun fibers have shown great potential applications in various fields.[5–9] Generally, the process of electrospinning is as follows. A charged polymer solution or melt jet is bending, branching, and whipping in a high electric field due to the interplay between the electric force and the solution surface tension.[10–13] With the solvent evaporating or melt cooling, the jet solidifies into fibers and deposits on the collector. Owing to the bending instability of the electrospinning jet, fibers with nonwoven and randomly arranged structures are the most typical macroscopic organization obtained.[12] However, the microstructures of the electrospun mats and even individual fiber can be designed and controlled by modifying the electrospinning devices and controlling the electrospinning process.[1–5,12,13]

It has been reported that ultrathin fibers with different structures (e.g., highly aligned arrays,[14–18] patterned mats,[19,20] crossed arrays,[21,22] and twisted fiber ropes[22,23]) can be electrospun by using special collectors such as rotating disk collectors,[14] parallel electrodes,[15] dielectric collector,[16] conductive pattern template,[19] frame collector,[23] or by centrifugal electrospinning[22] and near-field electrospinning.[24] Meanwhile for individual fibers with helical,[25,26] core–shell,[27] and hollow[28,29] structures, they could be obtained through modified electrospinning devices including reciprocating-type electrospinning,[25] electrospinning with tip collector,[26] and coaxial spinneret,[27–29] respectively. Moreover, by changing the electrospinning processing parameters (such as polymer materials, solution concentration, spinning voltage, working distance, and solution feeding rate), fibers with bead,[30,31] porous,[31,32] and ribbonlike[33,34] structures have also been successfully obtained.

Joachim in 1998 first obtained fibers with a closed-loop structure by drawing a single nanofiber.[35] It was reported that a closed-loop with a radius of 60 nm was formed by joining side-by-side two parts of open loops. Koombhongse *et al.* found loops formed in a single jet of polyhydroxyethyl methacrylate due to the bending and branching of the electrospinning process.[33] Moreover, by electrospinning, Reneker *et al.* have obtained a fluffy, columnar network of polycaprolactone (PCL) fibers named "garland".[36] The garland structure is formed by the constrained motion of some closed-loop fibers. It was pointed out that the closed-loop is formed by the contact of open loops in flight when the mechanical forces overcome the repulsive forces in the charged jets.[36] However, the preparation and formation mechanism of electrospun fibers

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†These two authors contributed equally to this work.

‡Corresponding author. E-mail: yunze.long@163.com

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with new closed-loop structure remains a challenge.

In this article, we report on a new closed-loop structure in individual cerium nitrate/polyvinyl alcohol ($Ce(NO_3)_3$/PVA) or NaCl/PVA fibers, which are fabricated by a modified electrospinning device with a tip collector. The electrospinning parameters such as voltage and solution concentration are controlled to examine the formation of the closed-loop structure. Additionally, the formation mechanism of the loop-like structure is also discussed.

2. Apparatus and experiments

As mentioned above, to fabricate fibers with controlled structures, modification of the electrospinning device is a common and effective method, and most of the modifications focus on the collector. Consequently, in this work, the modified electrospinning setup used is also a collector-modified one as displayed in Fig. 1(a), a metal nail is selected as the collector. The nail collector will concentrate the electrical field as shown in Fig. 1(b), which may enhance the bending and branching of the charged jet, and then fibers with curled structures may be obtained.[26]

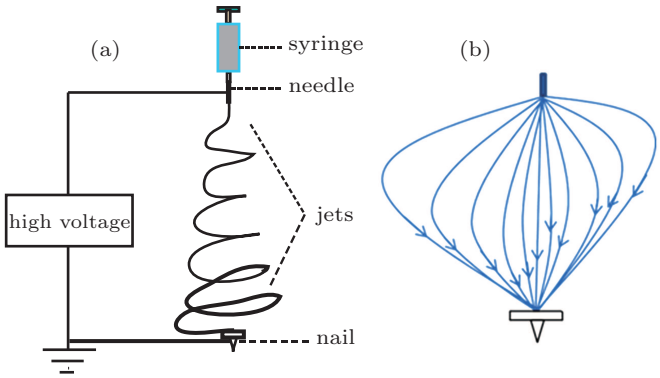


Fig. 1. (color online) (a) Schematic illustration of the modified electrospinning setup, where a metal nail is used as the collector. (b) The corresponding schematic electric field distribution.

The polymer solution was prepared by dissolving PVA (MW 60000, Sinopharm Chemical Reagent Co., Ltd., CHN) in deionized water at 10 wt.% and then stirring thoroughly for 2 h at room temperature. Subsequently, cerium (III) nitrate ($Ce(NO_3)_3{\cdot}6H_2O$, MW 434.22, Aladdin Industrial Inc., CHN) was dissolved in the prepared PVA solution at 1.5 wt.% for 2 h, then the $Ce(NO_3)_3$/PVA precursor solution with 1.5 wt.% $Ce(NO_3)_3$ was obtained. Similarly, $Ce(NO_3)_3$/PVA and NaCl/PVA solutions with different concentrations of the salt were prepared. All the solutions were agitated at room temperature under constant stirring for at least 24 h prior to electrospinning. The electrospinning was carried out under a high voltage of about 15–30 kV and the distance between the needle and the nail was about 10 cm at room temperature. The morphologies of the electrospun fibers were characterized by an optical microscope (BX-51, Olympus) and a zoom-stereo microscope (SMZ-168, Motic).

3. Results and discussion

3.1. Effect of electrospinning voltage on the formation of a closed-loop structure

It was suggested in our previous study that the tip collector electrospinning can produce fibers with curled structure.[26] As shown in Fig. 2, we successfully fabricate $Ce(NO_3)_3$/PVA fibers with the nail collector and the as-spun fibers do show some curled structures (see the enlarged image in Fig. 2(b)). Moreover, there is a closed-loop structure which arouses our interest. It is clearly shown in Fig. 2(c) that a closed-loop structure with a length of about 131.75 μm is obtained, and it seems that the individual fiber splits in the middle.

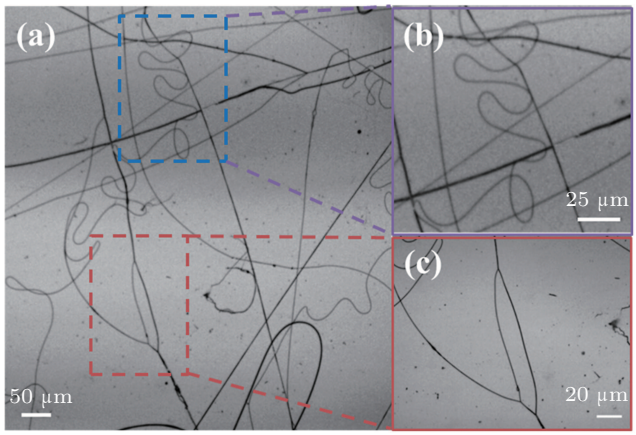


Fig. 2. (color online) (a) Optical image of the electrospun $Ce(NO_3)_3$/PVA fibers obtained with an applied voltage of 15 kV and under 10 cm distance. The enlarged two parts show (b) a fiber with a curled structure and (c) a closed-loop structure.

Table 1. Average diameters and loop structures of the electrospun $Ce(NO_3)_3$/PVA fibers obtained with different voltages.

Material	Voltage/kV	Diameter/μm	Loop number	Loop scale/μm
$Ce(NO_3)_3$/PVA	15	1.286±0.303	1	131.75
$Ce(NO_3)_3$/PVA	20	1.634±0.372	4	22.92±16.71
$Ce(NO_3)_3$/PVA	25	1.836±0.477	5	18.88±5.33
$Ce(NO_3)_3$/PVA	30	1.218±0.592	9	16.87±14.75

To investigate the formation of the closed-loop fiber, we first examine the effect of the applied voltage in the electrospinning process. Figures 3(a)–3(d) show the as-spun closed-loop fibers under the applied voltages of 15 kV, 20 kV, 25 kV, 30 kV, respectively. The electrospinning parameters and the as-spun fiber diameters, loop numbers, and loop scales are summarized in Table 1. As indicated in Fig. 3 and Table 1, the increase of the applied voltage results in the more representative numbers of the closed-loop structures. Moreover, the scale of the closed loop is reduced as the voltage increases. Owing to the increase of the voltage, the charged jet is driven

by an intensive electronic force, and the bending of the jet is enhanced.[26] Moreover, the charge carried by the electrospinning jet is raised and the Coulomb repulsion in the jet is strengthened, which may consequently result in the increase of the number of closed-loop fibers and the decrease of the loop scale.

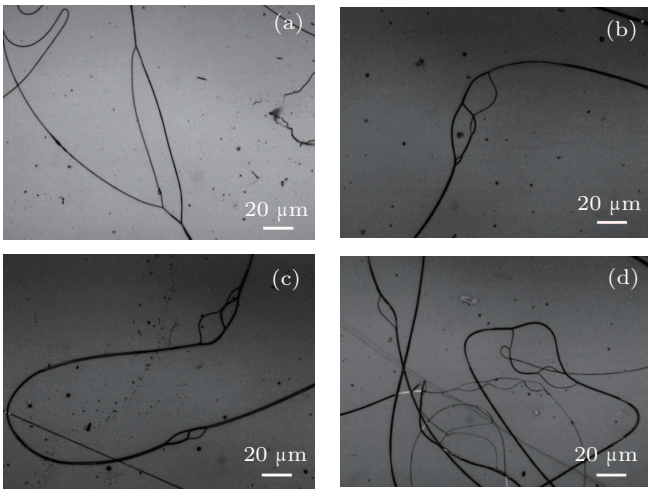


Fig. 3. Optical images of the electrospun $Ce(NO_3)_3$/PVA fibers with closed-loop structures obtained at a distance of 10 cm and the applied voltages of (a) 15 kV, (b) 20 kV, (c) 25 kV, and (d) 30 kV. The solution of $Ce(NO_3)_3$/PVA contains 1.5 wt.% $Ce(NO_3)_3$ and 10 wt.% PVA.

3.2. Effect of salt concentration on the formation of closed-loop fibers

It is mentioned above that a higher spinning voltage may induce the formation of closed-loop $Ce(NO_3)_3$/PVA fibers. For a further investigation, the PVA solutions with different concentrations of $Ce(NO_3)_3$ were prepared and the as-spun fibers were examined with an optic microscope as shown in Fig. 4. Table 2 summarizes the parameters of the electrospinning process and the as-spun fiber diameters and structures. It is suggested that the increasing concentration of $Ce(NO_3)_3$ does favor the formation of closed-loop fibers with increasing number of loops. Moreover, it is interesting that an individual continuous fiber with a number of closed-loops is caught in Fig. 4(c). Additionally, as the closed-loop fibers increase, the average loop scale also reduces and tends to be uniform. As is well known, the doping of the salt solution will increase the electrical conductivity of the solution,[17,32,34] the Coulomb repulsion between the charged ions in the solution will be enhanced accordingly,[34] and then splitting in the solution jets occurs, forming the closed-loop fibers.

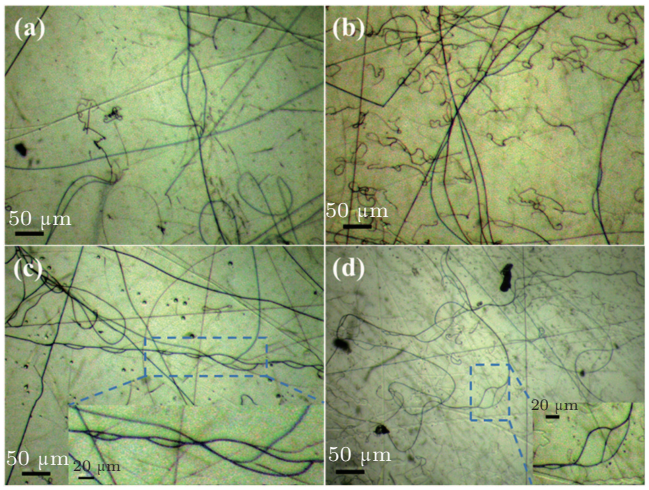


Fig. 4. (color online) Optical images of the electrospun closed-loop fibers obtained at a distance of 10 cm and an applied voltage of 30 kV with concentrations of $Ce(NO_3)_3$ of (a) 0 wt.%, (b) 1.0 wt.%, (c) 1.5 wt.%, and (d) 2.0 wt.%.

Table 2. Average diameters and loop structures of the electrospun $Ce(NO_3)_3$/PVA fibers obtained with different concentrations of $Ce(NO_3)_3$/PVA.

Material	Concentration /wt.%	Diameter/μm	Loop number	Loop scale/μm
PVA	10	1.19±0.275	2	81.55±56.79
$Ce(NO_3)_3$/PVA	1.0/10	1.28±0.251	3	60.32±35.51
$Ce(NO_3)_3$/PVA	1.5/10	1.31±0.189	8	48.04±24.59
$Ce(NO_3)_3$/PVA	2.0/10	1.502±0.206	13	30.53±18.66

Addition of $Ce(NO_3)_3$ to the PLA solution is beneficial for the formation of closed-loop structures and then a question is raised: whether the addition of other salts could also give a similar effect on the formation of close loops. Accordingly, an NaCl/PVA solution was prepared and then electrospun into fibers. The as-spun fibers are shown in Fig. 5. In accordance with expectation, the addition of NaCl is also favorable for the loop fibers despite less than that of $Ce(NO_3)_3$. These results suggest that the addition of a salt may introduce the formation of closed-loop structures in the electrospun fibers due to the increasing electrical conductivity of the solution with the doping of the salt.

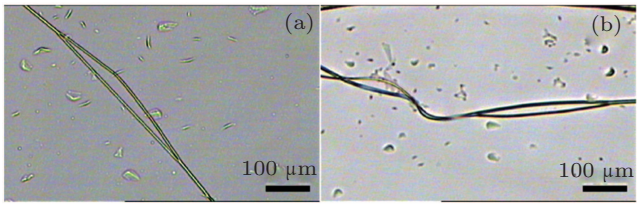


Fig. 5. (color online) Optical images of the electrospun NaCl/PVA fibers with the addition of NaCl at (a) 0.5 wt.% and (b) 1.0 wt.% under an electrospinning distance of 10 cm and an applied voltage of 25 kV at room temperature.

3.3. Mechanism of the formation of closed-loop structure

As mentioned in the introduction, electrospun fibers with closed-loop structure have been previously reported by Joachim[35] and Reneker *et al.*[33,36] Those closed-loop structures were usually formed by the side-by-side joining of two parts of open loops,[35] bending and branching of the electrospinning process,[33] or the contact of open loops in flight when the mechanical forces overcome the repulsive forces in the charged jet.[35] However, in this study, different closed-loop structures in a single fiber are observed, which is obtained from the salt doping PVA solutions by a tip electrospinning. As the experimental results suggest, the increases of the

high voltage and the concentration of the salt are favorable for the formation of closed-loop structures. This suggests another possible mechanism to explain the formation of closed-loop fibers. As shown in Fig. 6, the charged jet is bending in the electric field; due to the electrospinning device selected, the electric field tends to be intensive, which may strengthen the bending instability.[26] Moreover, the increase of the high voltage and the addition of the salt raise the charge carried by the single jet, and then the Coulomb repulsion plays a predominant role in the splitting of the individual fiber as described in Figs. 6(a)–6(c). Additionally, with the bending of the jet and solvent vaporization, fibers with closed-loop (Fig. 6(d)) can be obtained in the collector.

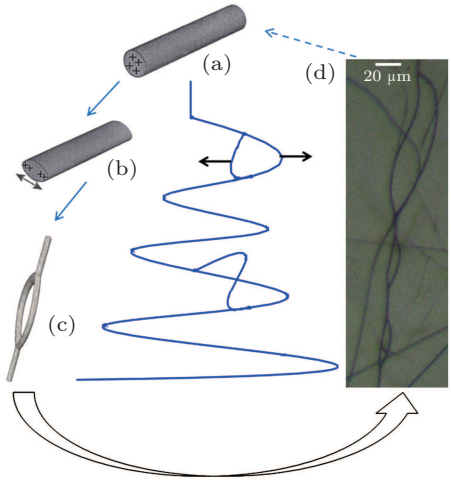


Fig. 6. (color online) Schematic illustration of electrospinning segment with closed-loop fiber and the model for formation of closed-loop structure. During the bending flight, the jet (a) is charged in the intensive electric field and the mutual repulsion is involved (b), the increasing Coulomb repulsion splits the jet in the middle, and then a closed-loop is formed (c). The closed-loop fibers are obtained on the collector (d).

4. Conclusion

We prepare $Ce(NO_3)_3$/PVA and NaCl/PVA composite fibers with closed-loop structure under high voltages and different concentrations of $Ce(NO_3)_3$ and NaCl by a tip electrospinning device. It is found that the increases of the voltage and the salt concentration will lead to the increase of representative number of closed loops and the decrease of the average scale of the closed loops. To understand the formation mechanism of the closed loop, a schematic model is proposed, in which the formation of the closed loop is ascribed to the Coulomb repulsion inside the single jet. The charge density of the electrospinning jet and thus the Coulomb repulsion can be enhanced by the intensive electric field from the designed tip electrospinning setup and the increase of the spinning voltage and the addition of salts.

References

[1] Huang Z M, Zhang Y Z, Kotaki M and Ramakrishna S 2003 *Compos. Sci. Technol.* **63** 2223
[2] Teo W E and Ramakrishna S 2006 *Nanotechnology* **17** R89
[3] Greiner A and Wendorff J H 2007 *Angew. Chem. Int. Edit.* **46** 5670
[4] Bhardwaj N and Kundu S C 2010 *Biotechnol. Adv.* **28** 325
[5] Lu W, Sun J and Jiang X 2014 *J. Mater. Chem. B* **2** 2369
[6] Liu C, Hsu P C, Lee H W, Ye M, Zheng G, Liu N, Li W and Cui Y 2015 *Nat. Commun.* **6** 6205
[7] Vijayakumar E, Subramania A, Fei Z and Dyson P J 2015 *RSC Adv.* **5** 52026
[8] Chen S, Yu M, Han W P, Yan X, Liu Y C, Zhang J C, Zhang H D, Yu G F and Long Y Z 2014 *RSC Adv.* **4** 46152
[9] Sun B, Long Y Z, Chen Z J, Liu S L, Zhang H D, Zhang J C and Han W P 2014 *J. Mater. Chem. C* **2** 1209
[10] Reneker D H, Yarin A L, Fong H and Koombhongse S 2000 *J. Appl. Phys.* **87** 4531
[11] Yarin A L, Kataphinan W and Reneker D H 2005 *J. Appl. Phys.* **98** 064501
[12] Reneker D H and Yarin A L 2008 *Polymer* **49** 2387
[13] Garg K and Bowlin G L 2011 *Biomicrofluidics* **5** 013403
[14] Theron A, Zussman E and Yarin A L 2001 *Nanotechnology* **12** 384
[15] Li D, Wang Y and Xia Y 2003 *Nano Lett.* **3** 1167
[16] Yan H, Liu L, Zhang Z 2009 *Appl. Phys. Lett.* **95** 143114
[17] Zhang Q, Wang L, Wei Z, Wang X, Long S and Yang J 2012 *J. Polym. Sci. B: Polym. Phys.* **50** 1004
[18] Wang S H, Wan Y, Sun B, Liu L Z and Xu W J 2014 *Nanoscale Res. Lett.* **9** 1
[19] Li D, Ouyang G, McCann J T and Xia Y 2005 *Nano Lett.* **5** 913
[20] Zhang D and Chang J 2007 *Adv. Mater.* **19** 3664
[21] Zussman E, Theron A and Yarin A L 2003 *Appl. Phys. Lett.* **82** 973
[22] Liu S L, Long Y Z, Zhang Z H, Zhang H D, Sun B, Zhang J C and Han W P 2013 *J. Nanomater.* **8** 2514103
[23] Lin D P, He H W, Huang Y Y, Han W P, Yu G F, Yan X, Long Y Z and Xia L H 2014 *J. Mater. Chem. C* **2** 8962
[24] Sun D, Chang C, Li S and Lin L 2006 *Nano Lett.* **6** 839
[25] Sun B, Long Y Z, Liu S L, Huang Y Y, Ma J, Zhang H D, Shen G Z and Xu S 2013 *Nanoscale* **5** 7041
[26] Tang C C, Chen J C, Long Y Z, Yin H X, Sun B and Zhang H D 2011 *Chin. Phys. Lett.* **28** 056801
[27] Sun Z, Zussman E, Yarin A L, Wendorff J H and Greiner A 2003 *Adv. Mater.* **15** 1929
[28] Li D and Xia Y 2004 *Nano Lett.* **4** 933
[29] McCann J T, Li D and Xia Y 2005 *J. Mater. Chem.* **15** 735
[30] Fong H, Chun I, Reneker D H 1999 *Polymer* **40** 4585
[31] Megelski S, Stephens J S, Chase D B and Rabolt J F 2002 *Macromolecules* **35** 8456
[32] Gupta A, Saquing C D, Afshari M, Tonelli A E, Khan S A and Kotek R 2008 *Macromolecules* **42** 709
[33] Koombhongse S, Liu W and Reneker D H 2001 *J. Polym. Sci. B: Polym. Phys.* **39** 2598
[34] Li M M, Long Y Z, Yin H X and Zhang Z M 2011 *Chin. Phys. B* **20** 048101
[35] Joachim C 1998 *Europhys. Lett.* **42** 215
[36] Reneker D H, Kataphinan W, Theron A, Zussman E and Yarin A L 2002 *Polymer* **43** 6785