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Direct Fabrication of Ultrafine Electrospinning Nanofiber

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Abstract: A novel spinneret assembled with Cu grid was presented in this paper to fabricate ultrafine nanofiber directly. Before electrospinning, hydrophobic treatment was performed on the Cu grid, which was then fixed at the front end of spinneret. During electrospinning, the polymer solution was transferred to the spinneret by the precise syringe pump. Through the holes in the Cu grid, polymer solution flow was divided into several smaller ones. The fine liquid flow from each hole of Cu grid was stretched into individual jets by the electric field force, and the liquid jets carried away the positive charges accumulated on the spinneret. Due to the hydrophobic treatment and the charge repulsive force between charged jets, liquid jets emanated from Cu grid kept their own tracks without aggregation. The initial diameter of liquid jet was greatly decreased by the Cu grid after hydrophobic treatment, and the smaller jet led to finer uniform nanofiber. Polyethylene oxide (PEO) and polyvinyl alcohol (PVA) ultrafine nanofiber with the diameter of 20—80 nm were fabricated by this novel spinneret, and the diameter of ultrafine nanofiber increases with the increase of polymer solution concentration.

Keywords: ultrafine nanofiber; electrospinning; spinneret; Cu grid; hydrophobic treatment

超细电纺纳米纤维的直接制备

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摘 要： 采用装配有疏水铜网的新型喷头研究了超细纳米纤维的制备. 静电纺丝实现之前，首先对铜网进行了疏水处理，并将其安装于喷头前端. 静电纺丝过程中，聚合物溶液由精密注射泵输送至喷头处. 安装于喷头的铜网可将管道内的聚合物溶液分成多股细流从铜网网孔中流出. 从铜网网孔流出的溶液细流受电场力作用被拉伸成多股独立射流，并从喷头携带走聚集的正电荷. 受铜网表面疏水性和射流间电荷排斥力的影响，从铜网喷射出的多股射流都将保持其独立的轨迹而不会产生聚集. 疏水铜网有利于减小纺丝射流的初始直径，并获得均匀的超细纳米纤维. 利用新型的电纺丝喷头成功制备了直径 20 ~ 80 nm 的聚氧化乙烯(PEO)和聚乙烯醇(PVA)超细纳米纤维. 实验结果表明，超细纳米纤维的直径随着电纺丝溶液浓度的增加而变大.

关键词： 超细纳米纤维; 静电纺丝; 喷丝头; 铜网; 疏水处理
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Electrospinning nanofibers, whose diameters range from tens of nanometers to a few micrometers, have received great attention from all over the world. With the unique characteristics of small diameter, large specific surface area and superior mechanical properties, electrospun nanofibers have been successfully applied to many application fields, such as filtration membrane [1], composite reinforcement [2] and bio-scaffolds [3]. Due to the unstable motion process of being charged, it is difficult to control the deposition position and diameter distribution of nanofiber. With the application of electrospinning technology in the micro/nano system integration, uniform nanofibers with the diameter of less than 100 nm are urgently required for the fabrication of micro/nano electrical, optical, mechanical and biomedical elements [4-6].

Since the electrospinning process is influenced by lots of factors and difficult to be controlled, the fabrication of uniform nanofiber with ultrafine diameter is still a great challenge for the application of electrospinning technology. Several analytical models based on electrohydrodynamic theory have been proposed to predict the ultimate diameter of electrospun nanofiber [7-9], and it is found that the initial jet/orifice diameter is one of the most significant factors affecting the radius of electrospinning jet. Experimental and theoretical analysis results show that the fine diameter of electrospinning jet is the most important factor in defining the ultrafine nanofiber [10]. At present, adding inorganic salts to the polymer liquid solution is the common way to decrease the diameter of electrospinning jet and electrospun nanofiber [11]. The solution conductivity increases with the increase of the inorganic salt concentration in polymer solution, which also decreases the diameter and diameter range of electrospun nanofiber [12]. Adding inorganic salt is an easy way to gain ultrafine nanofiber from electrospinning, but the addition of salts will change the properties of polymer solution and limit its application.

Fang *et al* [13] found that electrospinning jet was thinned at the early stage of whipping instability, and its uniformity was mainly improved at the later stage. Many experiments have shown that multi-jet ejection is beneficial for enhancing the whipping instability of charged jets and increasing the stretching ratio of nanofiber [14], which provides a potential way to fabricate ultrafine nanofiber. Presently, multi nozzles (inner diameter 50 μm—300 μm) [15] and surface spinneret (plate electrode [16] or circular cylindrical electrode [17]) are the most common methods for forming multi-jet ejection. Due to the larger initial diameter of Taylor cone emanated from the nozzle spinneret and the surface spinneret, it is difficult to fabricate uniform ultrafine nanofiber (diameter of less than 100 nm) by these methods.

There are small holes (hole size 30 μm—40 μm) in the Cu grid that is used to hold samples in transmission electron microscope (TEM). The solution flow can be divided into several smaller ones through the Cu grid and stretched into multi finer jets. But these solution flows will aggregate together again on the surface and form a single liquid jet with a larger diameter due to the hydrophilic surface of Cu grid. Multi-jet ejection and fine jets cannot be gained from the hydrophilic Cu grid spinneret. In this paper, hydrophobic treatment was performed on the Cu grid to prevent the aggregation of polymer solution on the surface. The fine solution flows can be stretched into individual jets by the electric field force without aggregation and form multi-jet ejection. Thanks to the multi-jet ejection and the fine jets, ultrafine nanofiber with the diameter of 20 nm—80 nm can be gained from the novel Cu grid spinneret.

1 Experiment

Firstly, the surface hydrophobic treatment of Cu grid (400 mesh, hole size 38 μm, thickness 30 μm, outer diameter 3.05 mm, Beijing XXBR Technology Co., Ltd., China) was done before electrospinning experiment. The process of hydrophobic treatment was as follows: ① Ultrasonic clearing in ethanol for 0.5 h; ② Drying in hot air flow (at 60 ℃) for 10 min; ③ Immersing in dodecafluoroheptyl-propyl-trimethoxylsilane ($C_{13}F_{12}H_{18}SiO_3$, Harbin Xeogia Fluorine-Silicon Material Co., Ltd., China) for 1 h; ④ Heating in vacuum heater (at 140 ℃) for 1 h. After the surface hydrophobic treatment, Cu grid was fixed on the end of flow pipe as electrospinning spinneret. The contact angle of deionized water droplet on the Cu grid surface without hydrophobic treatment was 88°, and that on the hydrophobic Cu grid surface increased to 105°, as shown in Fig. 1.

Polyethylene oxide (PEO, average molecular weight is 300 000 g/mol, Dadi Fine Chemical Co., Ltd., China) and polyvinyl alcohol (PVA, polymerization degree is 1 800, Dahao Fine & Special Chemical Products Co., Ltd., China) solutions were used as electrospinning ma-

terials in this paper. PEO was dissolved in a blending solution of 60% (volume fraction) deionized water and 40% (volume fraction) ethanol with the concentration of 10%—18%. PVA was added to deionized water and the solution concentration was 7%—9%. PVA and deionized water blend was stirred at the temperature of 95 ℃ for 2 h to make sure full dissolution of PVA powder.

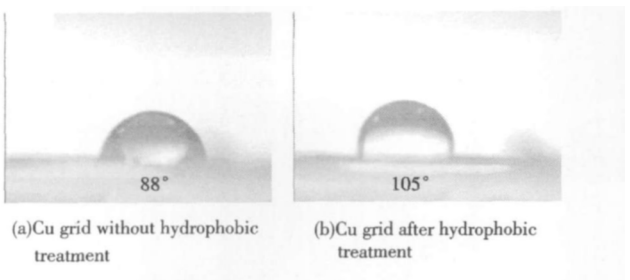


Fig. 1　Deionized water drop on the surface of Cu grid

Experimental setup was shown in Fig. 2. Polymer solution in syringe was transferred to the spinneret by precise syringe pump (Harvard 11 Pico Plus, USA). The anode of high potential power supply (DW-P403-1AC, Tianjin Dongwen High Voltage Power Supply Plant, China) was connected to polymer solution in the flow pipe, and the cathode was connected to the ground silicon substrate. The inner and outer diameters of solution pipe were 0.6 mm and 2 mm, respectively. Both Cu grid without hydrophobic treatment and steel nozzle with the inner diameter of 232 μm were used in this electrospinning system as comparative experiments, respectively.

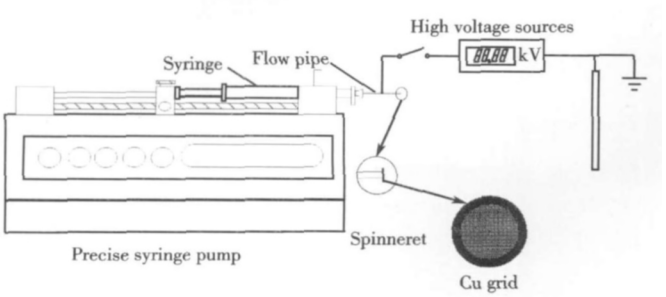


Fig. 2　Electrospinning setup with Cu grid

The polymer solution was filled into the syringe and fixed on the precise syringe pump. During the electrospinning experiment, switch of high voltage sources was turned on first before the polymer solution was transferred to the spinneret, by which solution assembly on the Cu grid surface can be avoided. And then, the precise syringe pump was turned on and the polymer solution was transferred to the spinneret. The liquid jets emanated from spinneret were recorded by high speed camera (GX-1, NAC Image Technology Inc, Japan). In this electrospinning experiment, the applied voltage, the distance from spinneret to collector and the flow rate were 10 kV, 10 cm and 30 μL/h, respectively.

2　Results and discussion

Under high voltage, liquid jets emanated from the three spinnerets were shown in Fig. 3.

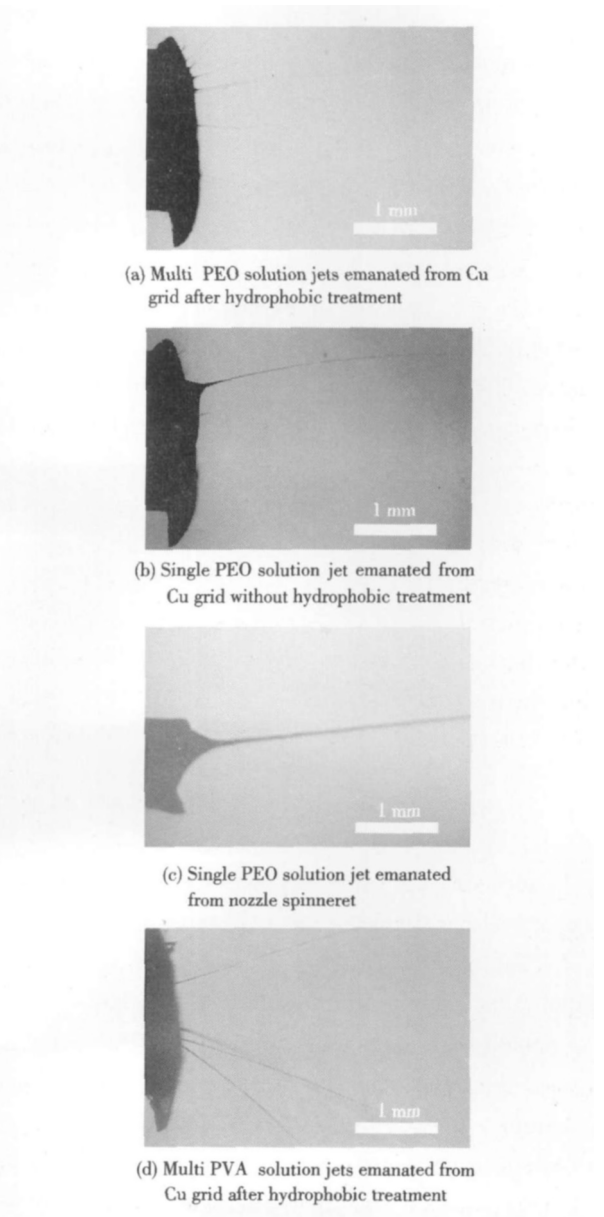
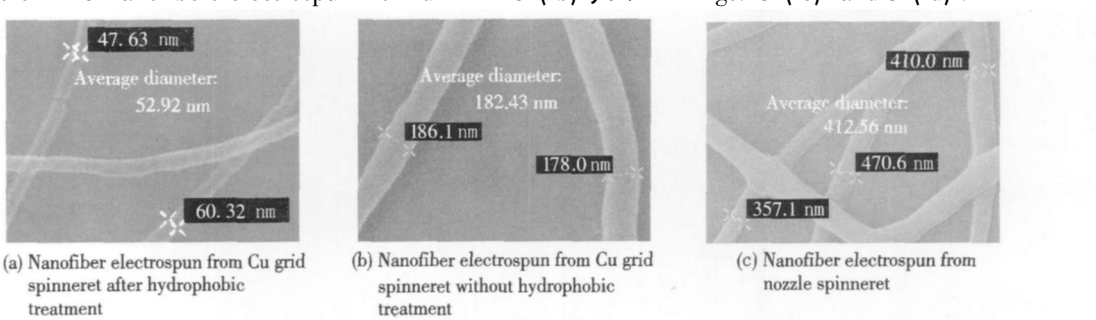


Fig. 3　Liquid jets emanated from different spinnerets

The solution flow was divided into several finer ones through the Cu grid, and stretched into individual charged jet by the electric field force. Multi-jet emanated from the hole of Cu grid after hydrophobic treatment kept their own tracks without aggregation (Fig. 3 (a)). But the polymer solution would aggregate on the surface of Cu grid without hydrophobic treatment and only one liquid jet was emanated from the Cu grid spinneret (Fig. 3 (b)), whose diameter was larger than that emanated from the Cu grid after hydrophobic treatment. When steel nozzle was used as the spinneret, the initial diameter of Taylor cone was supposed to be equal to the inner diameter of spinneret [18]. The jet diameter from nozzle spinneret (Fig. 3(c)) was larger than that from the other two spinnerets. Experimental results showed that hydrophobic Cu grid played a positive role in decreasing the initial diameter of electrospinning jet. In Figs. 3 (a)—(c), the PEO solution concentration was 14%. When PVA solution was used as electrospinning solution, multi-jet also formed from the Cu grid after hydrophobic treatment, as shown in Fig. 3(d). And the concentration of PVA solution was 9% in Fig. 3(d).

SEM images of PEO nanofibers electrospun from different spinnerets were shown in Fig. 4. The diameter of nanofiber gained from the Cu grid after hydrophobic treatment was much smaller than that gained from the other two spinnerets. According to the theoretical models [7-9], smaller jet usually leads to finer nanofiber. On the other hand, the charge repulsive force between liquid jets enhanced the whipping instability that further decreased the diameter of nanofiber. Under the same experimental condition, the average diameter of PEO nanofiber gained from the Cu grid spinneret after hydrophobic treatment was 52.92 nm (Fig. 4 (a)), that from the Cu grid spinneret without hydrophobic treatment was 182.43 nm (Fig. 4 (b)) and that from the nozzle spinneret was 412.56 nm (Fig. 4 (c)). In Fig. 4, the polymer solution concentration was 16%. PVA ultrafine nanofiber fabricated from the Cu grid spinneret after hydrophobic treatment with different polymer solution concentrations was shown in Figs. 5 (a)—(c). The diameter of PVA ultrafine nanofiber was within the range of 20—80 nm, while the average diameter of PVA nanofiber gained from nozzle spinneret was 260.97 nm (Fig. 5 (d)). The polymer solution concentration was 7% in Fig. 5 (a), 8% in Fig. 5 (b), 9% in Figs. 5 (c) and 5 (d).



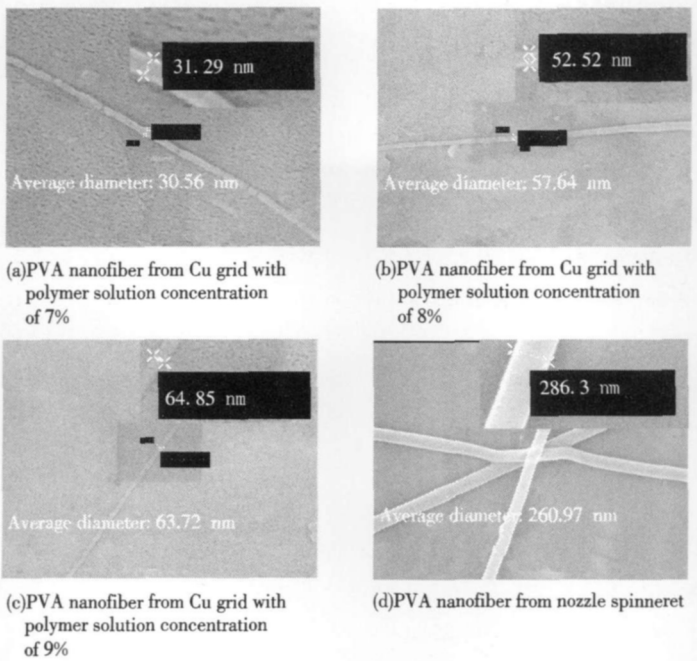
(a) Nanofiber electrospun from Cu grid spinneret after hydrophobic treatment

(b) Nanofiber electrospun from Cu grid spinneret without hydrophobic treatment

(c) Nanofiber electrospun from nozzle spinneret

Fig. 4 SEM images of PEO electrospun nanofiber

In addition, the effect of polymer solution concentration on nanofiber diameter was investigated, as shown in Fig. 6. The solution viscosity increases with the increase of solution concentration, which will lead to larger diameter of nanofiber. The average diameter of PEO nanofiber increased from 41.64 nm to 59.15 nm when the solution concentration increased from 10% to 18%. As PVA solution concentration increased from 7% to 9%, the average diameter of ultrafine nanofibers increased from 30.56 nm to 63.72 nm. The charge repulsive force between liquid jets emanated from the Cu grid spinneret enhanced the whipping instability, which improved the uniformity of nanofibers and decreased the diameter of nanofiber. And the diameter distribution of ultrafine nanofiber gained from the Cu grid spinneret after hydrophobic treatment was shown in Fig. 7. The diameter distribution range of nanofiber gained from nozzle spinneret in traditional electrospinning was wider than 100 nm [19]. The diameter distribution range of ultrafine nanofiber was only about 30 nm, which was much narrower than that gained from traditional electrospinning. The concentration of PEO solution was 10% in Fig. 7 (a), and the concentration of PVA solution was 9% in Fig. 7 (b).



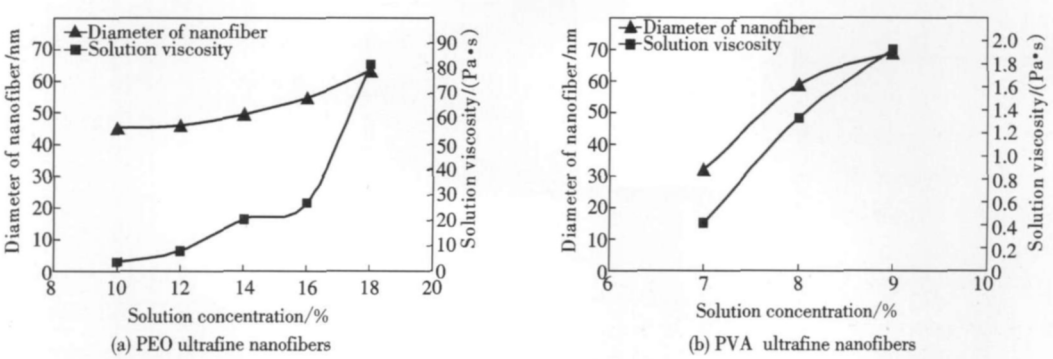
(a)PVA nanofiber from Cu grid with polymer solution concentration of 7%

(b)PVA nanofiber from Cu grid with polymer solution concentration of 8%

(c)PVA nanofiber from Cu grid with polymer solution concentration of 9%

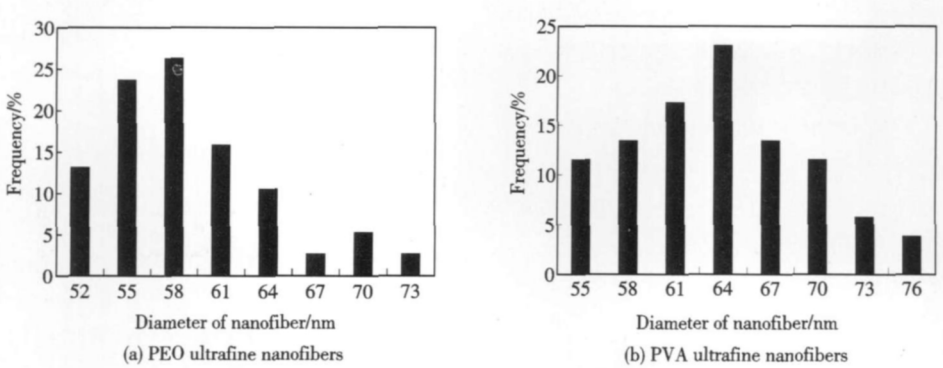
(d)PVA nanofiber from nozzle spinneret

Fig. 5　SEM images of PVA electrospun nanofiber



(a) PEO ultrafine nanofibers　　(b) PVA ultrafine nanofibers

Fig. 6　Effect of polymer solution concentration on the diameter of ultrafine nanofibers



(a) PEO ultrafine nanofibers　　(b) PVA ultrafine nanofibers

Fig. 7　Diameter distribution of ultrafine nanofibers

3　Conclusions

Cu grid after hydrophobic treatment was used as spinneret to fabricate ultrafine nanofiber. Solution flow from precise syringe pump was divided into several finer ones through the Cu grid, and stretched into individual jets by the electric field force. Owing to the hydrophobic surface, multi-jet from the novel Cu grid spinneret kept their own tracks without aggregation, and the diameter of

electrospinning jets was decreased greatly. Liquid jets ejected from the spinneret carried away the accumulated charges, and the charge repulsive force increased the whipping instability and further decreased the diameter of nanofiber. The whipping instability of multi-jet also improved the uniformity of ultrafine nanofiber. Taking the advantages of multi-jet ejection and finer diameter of liquid jet, uniform ultrafine nanofiber of PEO and PVA with the diameter of 20 nm—80 nm can be fabricated by this novel method. Experimental results show that the diameter of nanofibers increases with the increase of polymer solution concentration.

References:

[1] Heikkila P, Taipale A, Lehtimaki M, et al. Electrospinning of polyamides with different chain compositions for filtration application [J]. *Polymer Engineering and Science*, 2008, 48(6): 1168-1176.

[2] Liu L Q, Eder M, Burgert I, et al. One-step electrospun nanofiber-based composite ropes [J]. *Applied Physics Letters*, 2007, 90(8): 083108-1-3.

[3] Meechaisue C, Wutticharoenmongkol P, Waraput R, et al. Preparation of electrospun silk fibroin fiber mats as bone scaffolds: A preliminary study [J]. *Biomedical Materials*, 2007, 2(3): 181-188.

[4] Sun G E, Teng H, Zhang C L, et al. Preparation of ultrafine water-soluble polymers nanofiber mats via electrospinning [J]. *Chemical Research in Chinese Universities*, 2010, 26(2): 318-322.

[5] Wang Suqin, Yang Zhanhong, Li Hongbo, et al. H_2O_2-activated polyimide-based carbon nanofiber non-woven fabrics and their capacitances [J]. *Nanotechnology and Precision Engineering*, 2009, 7(3): 195-200(in Chinese).

[6] Zheng Gaofeng, Wang Lingyun, Sun Daoheng. Micro/nanostructure direct-write technology based on near-field electrospinning [J]. *Nanotechnology and Precision Engineering*, 2008, 6(1): 20-23(in Chinese).

[7] Feng J J. Stretching of a straight electrically charged viscoelastic jet [J]. *Journal of Non-Newtonian Fluid Mechanics*, 2003, 116(1): 55-70.

[8] Spivak A F, Dzenis Y A, Reneker D H. A model of steady state jet in the electrospinning process [J]. *Mechanics Research Communications*, 2000, 27(1): 37-42.

[9] Thompson C J, Chase G G, Yarin A L, et al. Effects of parameters on nanofiber diameter determined from electrospinning model [J]. *Polymer*, 2007, 48(23): 6913-6922.

[10] Zhao Congtao, Qin Xiaohong, Li Ni, et al. Effect of different salts on PAN electrospinning [J]. *Journal of Donghua University: Natural Science*, 2008, 34(1): 33-37(in Chinese).

[11] Yang D Y, Wang Y, Zhang D Z, et al. Control of the morphology of micro/nanostructures of polycarbonate via electrospinning [J]. *Chinese Science Bulletin*, 2009, 54(17): 2911-2917.

[12] Fukushima S, Karube Y, Kawakami H. Preparation of ultrafine uniform electrospun polyimide nanofiber [J]. *Polym J*, 2010, 42(6): 514-518.

[13] Fang J A, Wang H X, Niu H T, et al. Evolution of fiber morphology during electrospinning [J]. *Journal of Applied Polymer Science*, 2010, 118(5): 2553-2561.

[14] Varesano A, Carletto R A, Mazzuchetti G. Experimental investigations on the multi-jet electrospinning process [J]. *Journal of Materials Processing Technology*, 2009, 209(11): 5178-5185.

[15] Yang Y, Jia Z D, Li Q A, et al. A shield ring enhanced equilateral hexagon distributed multi-needle electrospinning spinneret [J]. *IEEE Transactions on Dielectrics and Electrical Insulation*, 2010, 17(5): 1592-1601.

[16] Zhou F L, Gong R H, Porat I. Polymeric nanofibers via flat spinneret electrospinning [J]. *Polymer Engineering and Science*, 2009, 49(12): 2475-2481.

[17] Wu D Z, Huang X P, Lai X T, et al. High throughput tipless electrospinning via a circular cylindrical electrode [J]. *Journal of Nanoscience and Nanotechnology*, 2010, 10(7): 4221-4226.

[18] Theron S A, Zussman E, Yarin A L. Experimental investigation of the governing parameters in the electrospinning of polymer solutions [J]. *Polymer*, 2004, 45(6): 2017-2030.

[19] Bellan L M, Craighead H G. Nanomanufacturing using electrospinning [J]. *Journal of Manufacturing Science and Engineering*, 2009, 131(3): 034001.