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Construction and Analysis of Probe Array Induced 3D Electrospun Nanofiber Structure

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Abstract: Three-dimensional (3D) nanofiber structure has vast potential applications due to its large surface area to volume ratio, controllable pore diameter and pore density. Probe array with adjustable height and position, which is controlled by switch controller to be connected with auxiliary voltage, is utilized as electrospinning collector. Desired 3D nanofiber structure can be fabricated by changing individual probe height, probe-to-probe distance and connectivity with auxiliary voltage. The preliminary experimental results show that the maximum/minimum of probe-to-probe distance decreases with the increase of applied voltage but increases with the increase of spinneret-to-collector distance. Meanwhile, auxiliary voltage decreases as spinneret-to-collector distance and probe-to-probe distance increase, but increases with the increase of height difference.

Keywords: 3D nanofiber structure; probe array; auxiliary voltage; electrospinning

探针阵列诱导构建三维电纺纳米纤维结构分析

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摘 要:三维纳米纤维结构具有超高比表面积、可控孔径和孔密度,潜在应用非常广泛. 以高度和位置可调的探针阵列为静电纺丝收集器,同时探针阵列通过控制开关与辅助电压相接,通过改变各探针高度、探针间距和与辅助电压的导通状态,制备所需的三维纳米纤维结构. 初步实验结果表明,最大/最小探针间距随着电压的增大而减小,而随喷头与收集器间距的增大而增大. 同时,增大探针高度差或减小喷头与收集器间距/探针间距将导致辅助电压变大.

关键词:三维纳米纤维结构; 探针阵列; 辅助电压; 静电纺丝
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Three-dimensional (3D) nanofiber structure has great application potential in composite materials, bioscaffold, energy and aviation etc[1]. A good example is that bone bioscaffold with proper aperture and porosity can accelerate bone regeneration[2]. At present, the bioscaffold fabrication methods such as 3D printing[3], phase separation[4], polymer foaming technique, particulate-leaching[5] and fused deposition modeling cannot meet the requirements of bioscaffold[6]. 3D structure of nanomaterials can greatly improve device performance[7]. Due to its simple setup and pure physical process, electrospinning, which can electrospin many materials such as polymer and ceramic nanofibers, has excited interest of more and more scientists[8]. Due to the low throughput of traditional electrospinning, scientists have invented many methods such as Nanospider, multi-

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porous tube spinning[9] and tip-less electrospinning[10] to greatly increase its production rate, which leads to electrospinning as a necessary choice. However, the intrinsic limitation of bending instability brings difficulties to the manipulation of electrospun nanofibers, thus only 2D in-macro nanofiber plane can be achieved[11]. Till now only quite little literature about 3D nanofiber fabrication has been reported. Zhang and Chang[12] used tubes as 3D collecting templates, which changes electrical field, to fabricate nanofibrous macroscopic 3D tubular structures with different microscopic architectures. Such a method can only fabricate a relatively simple structure with the same thickness. Zhang *et al*[13] utilized the modified collector composed of aluminum box, PMMA plate and aluminum foil to obtain 'bowl-like' structure, but it is difficult to control the size and only a bowl-shaped structure is gained. In this paper, a novel method that uses probe array with adjustable height difference, probe-to-probe distance and individual probe connectivity with auxiliary voltage as electrospinning collector, is brought forward to build up 3D electrospun nanofiber structures. And two main aspects at the beginning of 3D structure formation are investigated as follows: ① the effects of applied voltage and spinneret-to-collector distance on the maximum/minimum of probe-to-probe distance; ② the effects of height difference, probe-to-probe distance and spinneret-to-collector distance on auxiliary voltage.

1 Experimental details

The setup of 3D electrospun nanofiber structure consists of six components, as shown in Fig. 1: syringe pump, syringe, high voltage potential, probe array collector, switch controller and auxiliary voltage potential. A high voltage potential with the operating voltage ranging from 0 to 40 kV and the resolution of 0.1 kV is used. The syringe pump (Harvard 11 PLUS, USA) is utilized to drive working solution and the flux is set to be 160 μL. For ameliorating collector, height difference and probe-to-probe distance can be adjusted. The connectivity of each probe to auxiliary voltage potential (full range: 400 V) is controlled by switch controller and then each probe can be set to be auxiliary voltage or zero voltage, respectively, according to the desired structure.

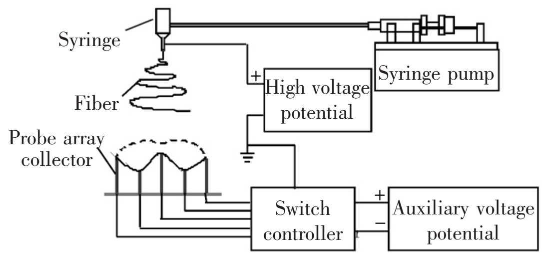

Fig. 1 Schematic setup of 3D electrospun nanofiber structure

Polyethylene oxide (PEO, average molecular weight = 300 kg/mol, Dadi Fine Chemical Co., Ltd., China) and deioned water/ethanol mixture as polymer solution were used. The solvent is composed of 80% (mass fraction) deioned water and 20% ethanol. Ethanol is used to accelerate evaporation rate in order to facilitate solidification of nanofibers. The typical concentration is 15% from our previous work[14]. Figs. 2 and 3 show the nanofibers on the 2×2 probe array and their pictures of scanning electron microscopy (SEM).

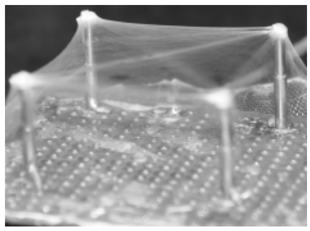

Fig. 2 Optical image of nanofibers deposited on 4 probe array collectors

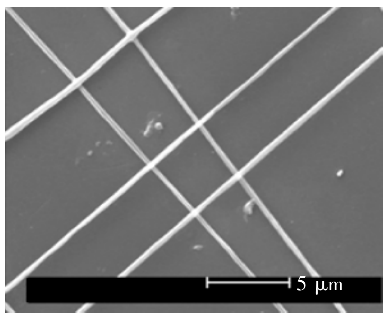

Fig. 3 SEM of PEO nanofibers

2 Results and discussion

The parameter of probe-to-probe distance is very crucial. When it is too large, fibers cannot spin linearly between the tips of the probes to form desired 3D structure and most of the fibers will gather on the tips of the probe. If the distance is reduced to be too small and the auxiliary voltage is zero, the nanofiber will not deposit onto the probe tips which are shorter than that next to them. The effects of applied voltage and spinneret-to-collector distance on probe-to-probe distance are investigated.

As illustrated in Fig. 4, when the applied voltage is regulated from 10 kV to 18 kV, the maximum probe-to-probe distance decreases from 1.9 cm to 1.7 cm under the height difference of 6 mm and the spinneret-to-collector distance of 15 cm. The same trend that the maximum probe-to-probe distance decreases with the increase of applied voltage can be found when the height difference is changed to 0 mm, 2 mm and 4 mm. It is believed that the trend is mainly due to the changed electric field at the probe tips. As is known, when the applied voltage is raised, the electric field strength at the probe tips is improved. Then the larger electric force from tips will prevent nanofiber from depositing onto the shorter probe tips. Finite element analysis results of the electric field elucidate that electric field strength increases with probe-to-probe distance. For example, under the simulation condition that the applied voltage, spinneret-to-collector distance and the height difference are 14 kV, 15 cm and 0 cm, respectively, the maximum electric field strength varies from 1.87×10^5 V/m to 2.04×10^5 V/m when the probe-to-probe distance shifts from 2.0 cm to 2.4 cm. Therefore, the probe-to-probe distance must be decreased to deposit the nanofibers onto the tip of each probe. At the same time, it can be seen that the larger the height difference is, the smaller the maximum distance will be. The reason is that as the height difference increases, the electric field strength of the shorter probe tips decreases and that of the probe tips next to them increases. For instance, the electric field at the shorter probe tips changes from 1.87×10^5 V/m to 1.16×10^5 V/m and that of the tips next to them from 1.87×10^5 V/m to 2.01×10^5 V/m when the height difference varies from 0 cm to 0.6 cm. Fig. 5 indicates that when the spinneret-to-collector distance is increased from 14 cm to 18 cm, the maximum of probe-to-probe distance will increase from 1.7 cm to 1.9 cm if the applied voltage and height difference are set to be 14 kV and 6 mm, respectively. Due to the same reason, the increase of spinneret-to-collector distance causes the decrease of electric field and the maximum of probe-to-probe distance should be increased.

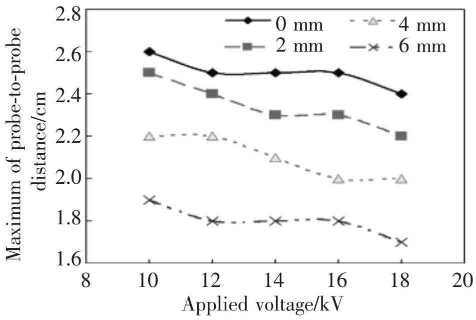

Fig. 4 Maximum of probe-to-probe distance versus applied voltage with different height differences (The spinneret-to-collector distance and the auxiliary voltage are 15 cm and 0 V, respectively)

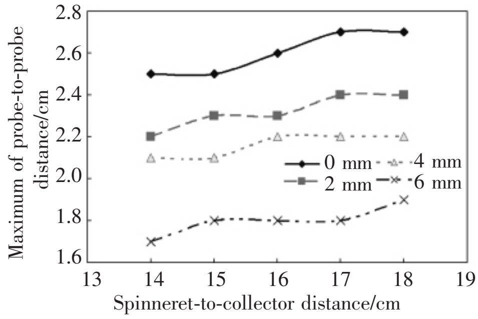

Fig. 5 Maximum of probe-to-probe distance versus spinneret-to-collector distance with different height differences (The applied voltage and the auxiliary voltage are 14 kV and 0 V, respectively)

Fig. 6 shows the relationship between the minimum of probe-to-probe distance and applied voltage. It is found that the minimum probe-to-probe distance decreases as the applied voltage increases. On the other hand, as the height difference changes from 2 mm to 6 mm, the minimum probe-to-probe distance increases. Obviously, larger height difference leads to a slimmer chance for nanofiber to travel to the shorter tips and the

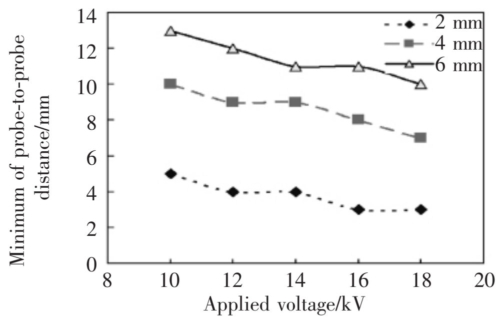

Fig. 6 Minimum of probe-to-probe distance versus applied voltage with different height differences (The spinneret-to-collector distance and the auxiliary voltage are 15 cm and 0 V, respectively)

probe-to-probe distance should be increased. As described in Fig. 7, as the spinneret-to-collector distance increases, the minimum distance will increase due to the decrease of electric field strength.

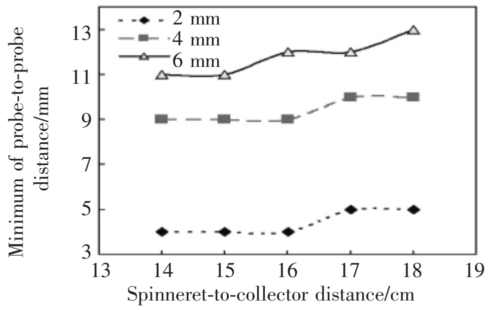

Fig. 7 Minimum of probe-to-probe distance versus spinneret-to-collector distance with different height differences (The applied voltage and the auxiliary voltage are 14 kV and 0 V, respectively)

However, in some desired 3D nanofiber structure whose surface projecting inside and curvature vary greatly (that is, some probes are much shorter than those next to them), the probe-to-probe distance should be less than the corresponding minimum of the probe-to-probe distance on the condition that all the probes are grounded. In order to achieve such a structure, positive auxiliary voltage is applied to higher probes to repel as-spun nanofibers to connect the shorter probes due to the changed electric field around. Then the effects of height difference, spinneret-to-collector distance and probe-to-probe distance on auxiliary voltage are explored.

Fig. 8 depicts the relationship between auxiliary voltage and height difference. It can be found that when the height difference changes from 3.0 mm to 4.5 mm, the auxiliary voltage increases from 89 V to 187.5 V. The auxiliary voltage increases with the height difference increasing. When the spinneret-to-collector distance, probe-to-probe distance, applied voltage and auxiliary voltage are 15 cm, 5 mm, 10 kV and 89 V, respectively, simulation results show that as the height difference increases from 3.0 mm to 4.5 mm, the electric field strength of the shorter probe tips changes from 1.24×10^5 V/m to 9.37×10^4 V/m but that of the probe tips next to them increases from 1.83×10^5 V/m to 1.96×10^5 V/m. On the other hand, the increase of the height difference weakens the possibility of reaching the shorter probe tips. For the height differences of 10 mm and 13 mm, the same trend is achieved. For the above two reasons, the auxiliary voltage has to be increased to strengthen the repellent force onto the nanofibers so that there is more chance for them to reach the probe tips. The effect of the probe-to-probe distance on the auxiliary voltage is also studied by changing the probe-to-probe distance from 8 mm to 11 mm, as described in Fig. 9. The auxiliary voltage decreases from 132.5 V to 90.5 V and 219 V to 141 V for the height differences of 5 mm and 6 mm, respectively. Experimental results in Fig. 10 show that when the spinneret-to-collector dis-

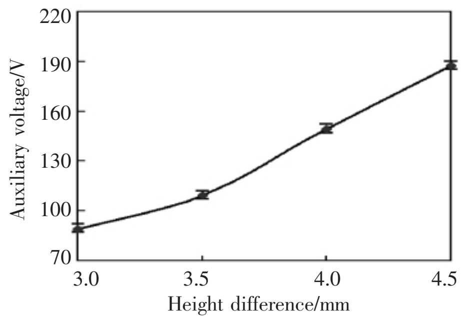

Fig. 8 Auxiliary voltage versus height difference (The spinneret-to-collector distance, the probe-to-probe distance and the applied voltage are 15 cm, 5 mm and 10 kV, respectively)

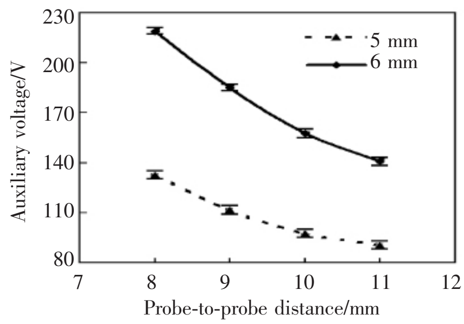

Fig. 9 Auxiliary voltage versus probe-to-probe distance with 5 mm and 6 mm height differences (The spinneret-to-collector distance and the applied voltage are 15 cm and 10 kV, respectively)

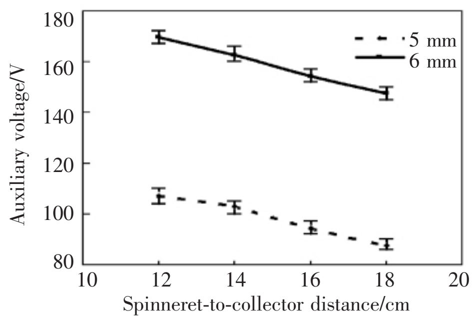

Fig. 10 Auxiliary voltage versus spinneret-to-collector distance with 5 mm and 6 mm height differences (The applied voltage and the probe-to-probe distance are 10 kV and 10 mm, respectively)

tance varies from 12 cm to 18 cm, the auxiliary voltage changes from 107 V to 88 V and 170 V to 148 V for the height differences of 5 mm and 6 mm, respectively.

3 Conclusion

Probe array is utilized as an electrospinning collector to successfully fabricate macroscopic 3D nanofiber structure and the connectivity of individual probe with auxiliary voltage potential is controlled by switch controller. The effects of applied voltage and spinneret-to-collector distance on the maximum/minimum of the probe-to-probe distance are explored. The experimental results show that the maximum/minimum of the probe-to-probe distance decreases with the increase of the applied voltage but the opposite trend is achieved for the spinneret-to-collector distance. From the experimental results, it can also be concluded that auxiliary voltage decreases with the increase of spinneret-to-collector distance and probe-to-probe distance, but increases with the increase of height difference. Such a method may open a new way to build up macroscopic 3D nanofiber structure in the future.

References:

[1] Xu C Y, Inai R, Kotaki M, et al. Aligned biodegradable nanofibrous structure: A potential scaffold for blood vessel engineering [J]. *Biomaterials*, 2004, 25(5): 877-886.

[2] Bonzani I C, George J H, Stevens M M. Novel materials for bone and cartilage regeneration [J]. *Current Opinion in Chemical Biology*, 2006, 10(6): 568-575.

[3] Michna S, Wu W, Lewis J A. Concentrated hydroxyapatite inks for direct-write assembly of 3-D periodic scaffolds[J]. *Biomaterials*, 2005, 26(28): 5632-5639.

[4] Keshaw H, Thapar N, Burns A J, et al. Microporous collagen spheres produced via thermally induced phase separation for tissue regeneration [J]. *Acta Biomaterialia*, 2010, 6(3): 1158-1166.

[5] Wang Zhen, Zhang Zheng, Zhuang Junchuan, et al. Distribution of bone marrow stem cells in large porous polyester scaffolds [J]. *Chinese Science Bulltin*, 2009, 54(17): 2968-2975.

[6] Chen Zhongzhong, Li Dichen, Lu Bingheng, et al. Fabrication of osteo-structure analogous scaffolds via fused deposition modeling [J]. *Scripta Materialia*, 2005, 52(2): 157-161.

[7] Ko S H, Lee D, Kang H W, et al. Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell[J]. *Nano Letters*, 2011, 11(2): 666-671.

[8] Huang Z M, Zhang Y Z, Kotaki M, et al. A review on polymer nanofibers by electrospinning and their applications in nanocomposites[J]. *Composites Science and Technology*, 2003, 63(15): 2223-2253.

[9] Dosunmu O O, Chase G G, Kataphinan W, et al. Electrospinning of polymer nanofibers from multiple jets on a porous tubular surface [J]. *Nanotechnology*, 2006, 17(4): 1123-1127.

[10] Wu Dezhi, Huang Xiaoping, Lai Xiting, et al. High throughput tip-less electrospinning via a circular cylindrical electrode[J]. *Journal of Nanoscience and Nanotechnology*, 2010, 10(7): 4221-4226.

[11] Gopal R, Kaur S, Ma Z W, et al. Electrospun nanofibrous filtration membrane [J]. *Journal of Membrane Science*, 2006, 281(1/2): 581-586.

[12] Zhang Daming, Chang Jiang. Electrospinning of three-dimensional nanofibrous tubes with controllable architectures[J]. *Nano Letters*, 2008, 8(10): 3283-3287.

[13] Zhang Jianfeng, Yang Dongzhi, Nie Jun. Preparation of three-dimensional structure controllable nanofibers by electrospinning [J]. *Polymers for Advanced Technologies*, 2008, 19(9): 1150-1153.

[14] Wu Dezhi, Wang Lingyun, Sun Daoheng. Patterned deposition of PEO nanofibers [C] //*The 4th IEEE International Conference on Nano/Micro Engineered and Molecular Systems*. Shenzhen, China, 2009: 584-587.

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