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Large-scale Patterned Nanofibers Via Tip-less Electrospinning

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***Abstract*- Tip-less Electrospinning (TLES) process has been developed to produce polymer nanofibers with high throughput. And the ameliorated collector with parallel top-down configurations of two different materials in conventional electrospinning, such as polyethylene terephthalate (PET)-glass, copper-glass and PET-silicon etc, can achieve patterned nanofibers to expand its future applications. In this paper such patterned collectors array with changed electric field around, are introduced to TLES to deposit large-scale patterned nanofibers. The experiment results show that patterned nanofibers can be collected along the gap between plastic plates in both plastic-glass and plastic-silicon configuration. To the copper-glass collector, nanofibers bridge over the gap and the nanofiber quantity density on the gap is much less than that on the copper. But the patterned effects in all configurations are relatively weaker than that from foremetioned spinning due to their much higher speed, more serious bending instability and repulsive interactions between as-spun nanofibers.**

Keywords*- *Tip-less electrospinning, large-scale, nanofiber, patterned deposition

I. INTRODUCTION

Due to its high surface area to volume ratio and distinguished properties (mechanical, electrical and optical), electrospun nanofibers will play important roles in future applications of reinforced material [1], high performance filters [2], tissue scaffolds [3, 4], drug delivery [5, 6], high-sensitivity sensor [7, 8], micro/nano electronic device [9] and so on. However the electrospun nanofibers are chaostic because of bending instabilities, which limits their applications of circuits, sensors and actuators, to name a few. On the other hand, there is only one spinneret and its throughput is only about 0.02g/h. Such will greatly increase its cost and hinder its industrial applications. So there are two key technology challenges: one is large-scale production, the other is patterned rather than random architechures of nanofibers. Scientists all over the world have invented lots of technologies to improve production speed or to achieve patterned deposition of nanofibers [10, 11]. For example, Theron utilized multiple spinnerets, which are arranged in one line or a matrix on a plane, to spin nanofibers simutaneously and models were used to describe the viscoelastic behavior of the polymer jets [12]. Another good example is that Wu *et al* placed circular cylindrical electrode which surface is coated a thin polymer solution with thickness 0.5mm to 2mm as a spinneret under a strong electric field to electropin nanofibers with throughout about 5.2g/h [13], which is named Tip-less Electrospinning (TLES). Sun invented a technique called near-field electrospinning to direct write nanofibers with controllable manner [14]. Another technique is invented by our group to pattern nanofibers, in which parallel top-bottom structure of two different materials is introduced as collectors to traditional electrospinning to change electric field around the collector [15]. But till now no literatures have reported that any methods can solve above two problems at the same time. In this paper, a novel method to obtain patterned nanofibers with high throughput is brought forward, in which ameliorated collectors with parallel top-down configurations of two different materials is introduced into tip-less electrospinning process.

II. EXPERIMENTS

Polyethylene oxide (PEO, average molecular weight = 300,000g/mol, Dadi Fine Chemical Co., Ltd., China) was used to prepare a solution that was used as the working fluid and the concentration is 15% from previous works. The solution was dissolved in room temperature. The setup of TLES consists of four components as shown in Figure 1A: a cylindrical-shape electrode, a scraper, a patterned collectors array and a high voltage supplier. Circular cylinders with diameters 50mm and 120mm in length made of either stainless steel have been successfully used as the tip-less electrode. The scraper is used to control the thickness of the deposited polymer solution. A high voltage power supply with operating voltage ranging from 0 to 120kV and resolution of 0.1kV is used. The patterned collectors array which consist of two thin parallel top plates (PET plastic or glass) with a gap and a bottom plate (glass or copper) lies on the ground copper meshes.All the samples are characterized by XL30 Field-Emission Environmental Scanning Electron Microscope (ESEM-FEG).

III. RESULTS AND DISCUSSIONS

When enough high voltage is applied to the cylindrical electrode, several jets are generated during the process and it is hard to estimate the exact number. The bases of liquid jets as illustrated in Figure 1B move randomly during the process with a speed of 0.3~1mm/s in favor of high electrical field areas, which had been testified with artificial tips to generate the highest electric field to attract the bases of jets.

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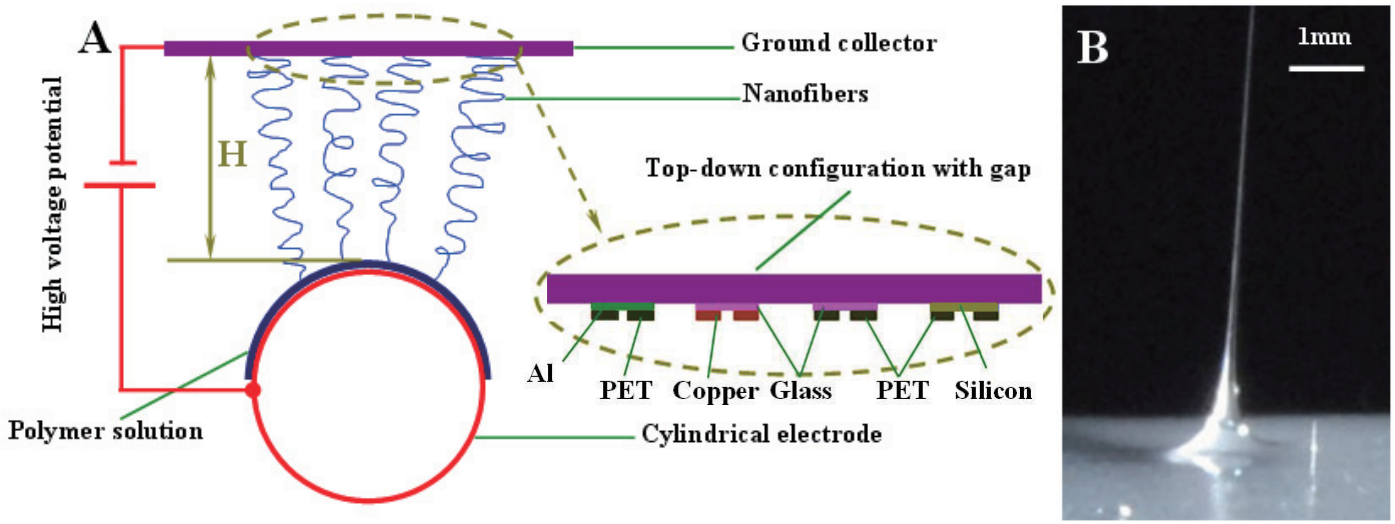

Fig.1 (A) Schematic diagram of tip-less electrospinning system setup; (B) Optical view of a single jet and its base.

In order to get patterned nanofibers, the parallel top plates and the bottom plate are set to be plastic and silicon respectively. As shown in Figure 2, chaotic and bended fibers with diameter of 175nm gathered on the 740μm-width gap between PET and they are much denser than that on PET. As shown in Figure 2B, the nanofibers on the PET are nearly straight. At the PET corner (Fig.2C), most nanofibers are parallel and perpendicular the bisector of the angle. At the gap corner the fibers begin to disperse and the edge of the fibers deposition looks like two arcs near the corners of the plastic plates, which is the same to that from single-tip patterned electrospinning. At initial stage the deposition of nanofibers is somewhat parallel along the gap (Fig.2D). The reason is that the as-spun positively charged nanofiber encounters strongly repulsive electrical force from PET, which can attract positive charges, and attraction forces from silicon. Thus the nanofibers near the gap are stretched and repelled to the silicon gap. Then the as-spun fibers on the gap mainly suffer attraction forces from the negative charges on the silicon substrate and the positive charges continue to stretch them. So at first the nanofibers is parallel in some extent. With more and more nanofibers depositing onto the silicon, the positive charges on the fibers also affact the as-spun nanofibers and they encounter more complex forces, thus the fibers become bended and chaotic. Fibers deposit upto the PET corner because of insufficient time for fibers to fly to gap. To the nanofibers onto the PET plate, they are stretched all the time before landing, so they are all straight.

When the nanofibers rush the collector which is composed of PET on the parral top and glass at down, as depicted in Figure 3, most aligned nanofibers gathered on the 537μm-width gap between the parallel top plastic plates and the nanofibers on the gap is much denser than that on the plastic plate. To the nanofiber at the corner, they are more parallel than that at corner of PET-silicon collector. It is believed that the as-spun nanofibers suffer just repulsive forces from positive charges on the PET and the glass. Because the positive charges on the PET are much more than that on the glass, the fibers are also repelled onto the glass gap and stretched to rotate to the direction that the moment on the nanofibers becomes zero, that is, parallel to the gap. Furthermore, positive charges on the glass will help stretching the nanofibers and thus most of the fibers deposit orderly on the gap.

To the copper-glass collectors as shown in Fig.4, much different to that from PET-silicon and PET-glass collector, fibers bridge two ground copper over the gap and their number density along the gap is much fewer than that on copper plate. and fibers deposit disorderly and curledly on the copper. because its induced negative charges of the copper attract the as-spun fiber to their own side, then fibers rotates to the direction that the moment become zero, that is perpendicular to the gap edge of the copper plate. At the corner of copper plate shown in Figure 4C, the fibers piled together, which are much denser than that on other area. It is believed that due to its electric edge effect, more negative charges at the corner generate stronger attraction force on the as-spun nanofibers.

Compared to the patterned effect from single-tip electrospinning in literature [15], large-scale pattern can be achieved but the patterned effect is poorer because of (a) much higher moving speed; (b) more drastic bending instability and (c) repulsive electrical force from other as-spun nanofibers.

IV. Conclusions

In this paper ameliorated collectors array, which is composed of different types of parallel top-bottom configurations of two different materials, that is, plastic (PET)-silion, plastic (PET)-glass and copper-glass plates are introduced to TLES process to achieve patterned nanofibers with high throughput to patterned area to expand their applications. The experiment results demonstrate that most of the nanofibers can be gathered along the gap between PET plates in plastic-glass and plastic-copper configuration and the

fibers on the gap in plastic-glass is parall to the edge of PET plate because PET plate can attract and keep positive charges to strongly repel the positively charged nanofibers due to electro-negativity of oxygen of carbonyl group for PET and the positive charges help to stretch nanofibers. The nanofibers on the copper-glass collecter bridge over the gap and its number density is much fewer than other area due to attraction force from induced negative charges.

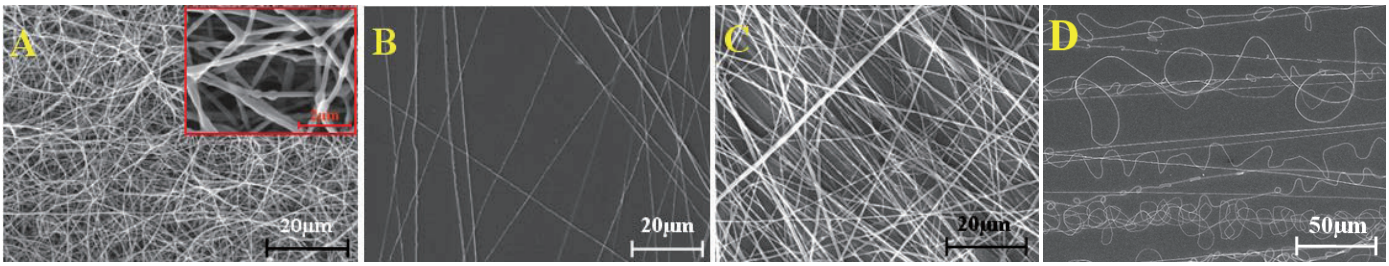

Fig. 2 SEM of nanofibers at different area of the PET-silicon collector (A) on the gap; (B) on the PET plate; (C) at the corner of the PET plate; (D) on the gap in another experiment. The reference experimental conditions are applied voltage of 60kV, electrode-to-collector distance of 20cm and electrode diameter of 50mm.

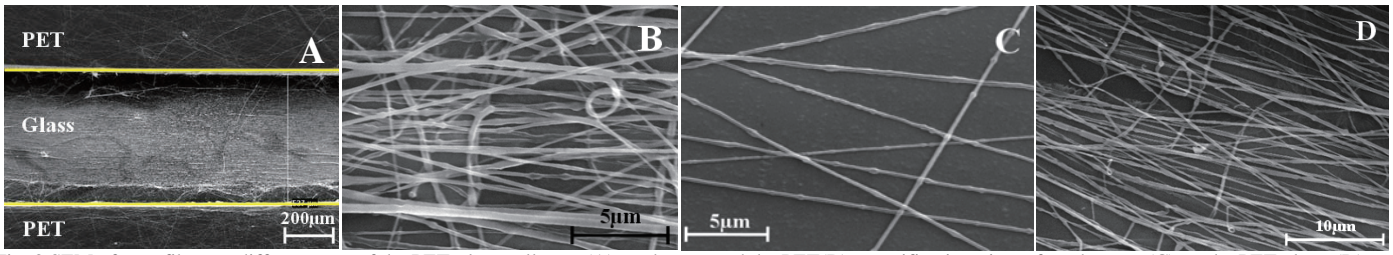

Fig. 3 SEM of nanofibers at different area of the PET-glass collector (A) on the gap and the PET(B) magnification view of on the gap; (C) on the PET plate; (D) at the corner of the PET plate;. The applied voltage, electrode distance, the electrode diameter and humidity is 60kV, 18cm, 50mm and 40%RH respectively.

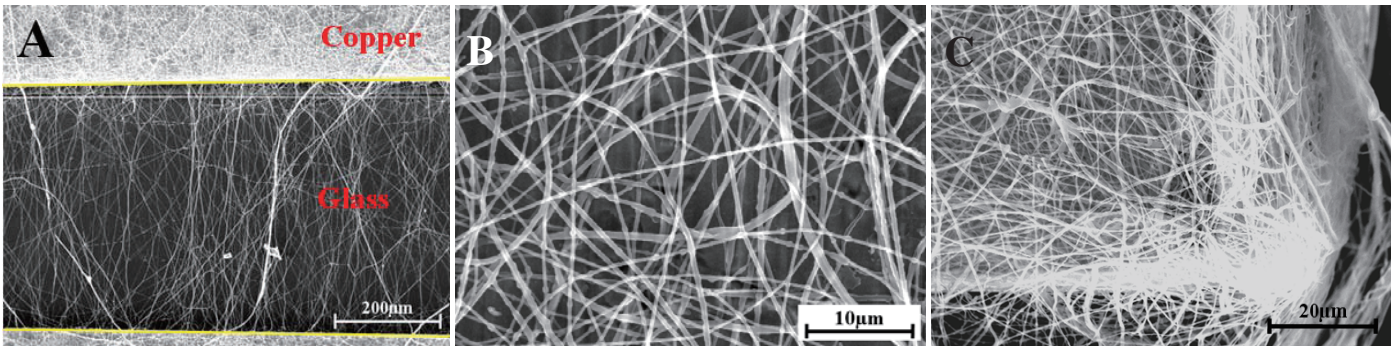

Fig. 4 SEM of nanofibers at different area of the copper-glass collector (A) on the gap and the two parallel top copper plates; (B) on the ground copper plate; (C) at the corner of the copper plate;. The applied voltage, electrode distance and the electrode diameter is 60kV, 18cm and 50mm respectively.

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