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Template-assisted assembly of electrospun fibers

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ABSTRACT

Ordinarily, the electrospinning process generates one-dimensional fibers which assemble into non-woven membrane structures due to instabilities in the fluid jet. In this paper, an electrospinning procedure is developed that utilizes patterned collectors to produce aligned membranes with designed topological structures. The template-assisted electrospinning approach is demonstrated using poly-caprolactone (PCL) fibers to produce patterns including alphanumeric characters and a printed electronic circuit chip, with feature sizes on the order of several hundred microns. The process has a significant impact on micro-manufacturing, and provides the capability for incorporation of oriented fiber materials in patterned micro-composites and electronic components.

1. Introduction

The process of electrospinning has attracted a great deal of attention over the past decade as a simple and versatile technique for producing fibers with diameters ranging from the micrometer scale down to the nanometer scale [1–3]. In a typical electrospinning setup, a liquid precursor is forced through a nozzle which is held at high voltage, causing the precursor to form electrically charged droplets at the tip of nozzle that initiate the ejection of electrospun jets. At a certain critical voltage, the charged jets undergo elongation and thinning to form one-dimensional fibers. Significant advances in this technique have been achieved over the past few years, allowing for the electrospinning of uniform fibers of a wide variety of materials that includes polymers, ceramics, metals, and organic–inorganic hybrid materials [4–6]. Electrospun fibers have applications in a diverse range of fields, such as biomedical engineering, filtration, electrical engineering, and optics [2,3,7–10].

Due to bending instabilities of the charged liquid jets, the electrospun fibers are generally deposited as non-woven, randomly assembled mats on the collector. However, it is desirable to control the spatial arrangement of the electrospun fibers to generate patterned structures which would enable the use of the electrospinning technique for a much broader array of applications. Specifically, the preparation of well-aligned fibers that have patterned structures is very important in fiber reinforced composites, electronic and photonic devices, and biomedical engineering applications [1–3,11–15]. Several groups have developed new approaches to collect aligned electrospun fibers. Near-field electrospinning is one approach, and other methods have been devised that use additional equipment such as auxiliary electric fields, rotating collectors, rotating drums and counter electrodes, and electrostatic lenses [16–21]. More recently, researchers have demonstrated that the patterning of electrospun fibers can be realized by using a specially designed collector consisting of patterned electrodes [22–24]. By designing an appropriate patterned electrode configuration the electrospun fibers can be collected and assembled into well-organized structures. In this communication, we report on the use of template collectors to guide the assembly of electrospun fibers into mats with tailored structural configurations, aimed at synthesizing useful materials for various industrial and biomedical applications.

2. Experimental

Fig. 1(a) shows a basic electrospinning setup, which consists of a high-voltage power supply (Sigma), syringe (BD company), nozzle (McMaster), syringe pump (Cole–Parmer), and a collector. Fig. 1 (b)–(e) show digital images of the substrate configurations used for the metal template collectors. The template-collector morphologies used were parallel gridlines, woven wires, regular hexagons, and circular holes, respectively. Generally, the materials of the collector are electroconductive, and the inter-space resolution of a collector with a special structure can not be too small due to the difficulty in the electrical-field-assisted selective deposition of electrospun fibers onto the template collectors. Poly(ϵ-

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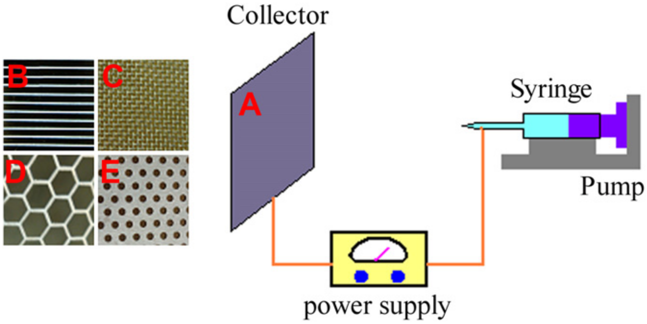

Fig. 1. Schematic illustration of an electrospinning setup and the digital images of the template collectors.

caprolactone) (PCL, Aldrich, average molecular weight: 80,000) was used as a model material to demonstrate the procedure. A precursor solution of 10 w/v% was prepared by dissolving PCL in a mixture of dichloromethane (Aldrich) and methanol (Aldrich) in a ratio of 4:1 by weight, followed by magnetic stirring for 2 h at room temperature. The precursor solution was then loaded in a 5 ml plastic syringe equipped with a 25 Gauge stainless steel nozzle connected to a high-voltage power supply capable of up to 30 kV. The solution was continuously pumped through the nozzle using a syringe pump at a constant flow rate of 3.0 ml/h. Typically, an applied voltage of 25 kV and an electrospinning distance of 18 cm were used. The morphology and microstructure of the electrospun mats and the patterned collectors were characterized using an optical microscope (Olympus BH-2), digital camera (Canon), and a field-emission scanning electron microscope (FE-SEM, Zeiss-Leo DSM982 model). The electrospun mats were coated with gold before SEM imaging.

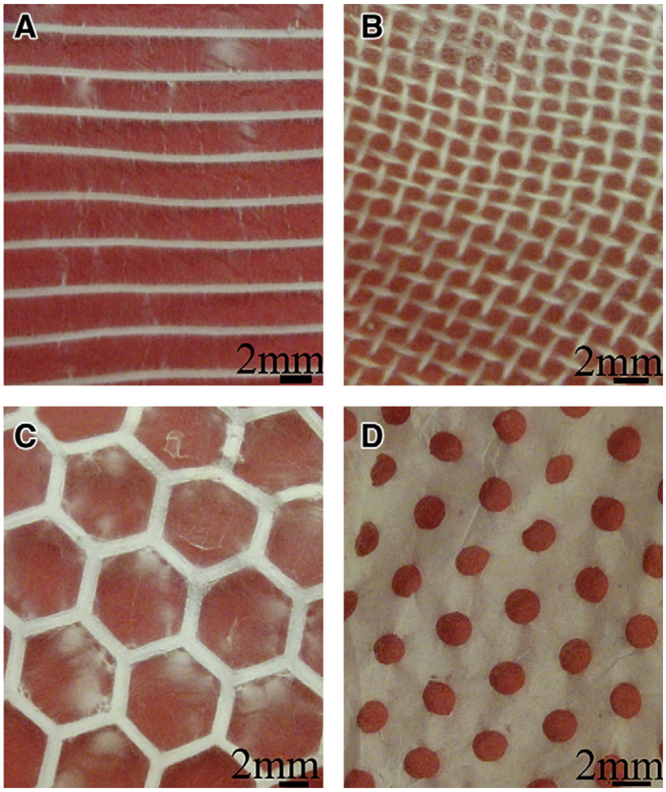

Fig. 2. Digital images of free-standing electrospun membranes with well-organized structures: (A) parallel lines; (B) woven lines; (C) regular hexagons, and (D) circular holes.

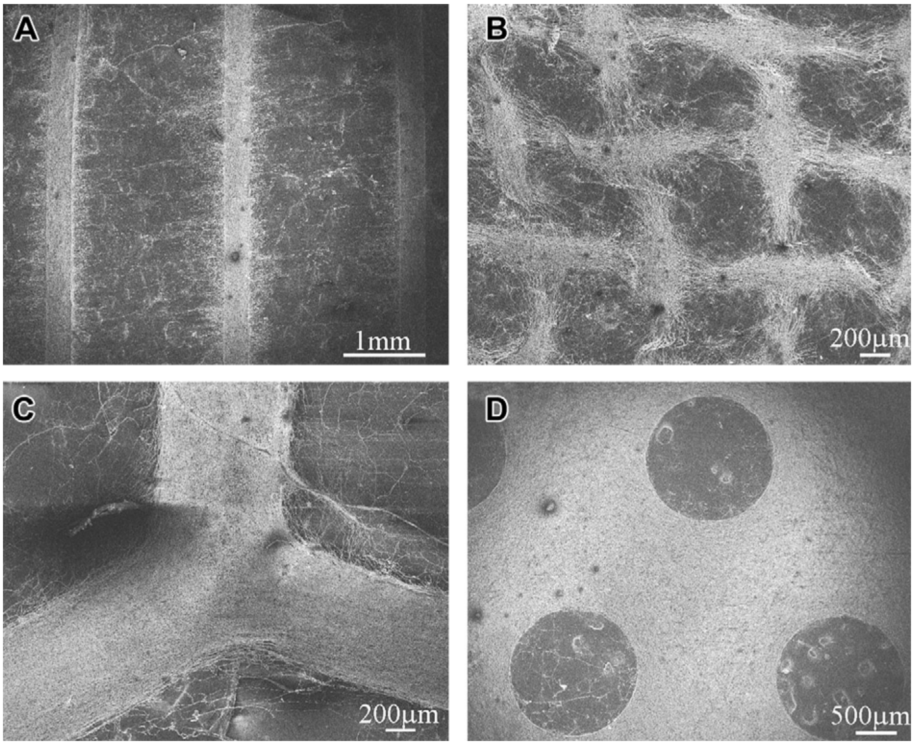

Fig. 3. SEM images of free-standing electrospun membranes generated using template collectors: (A) parallel structures; (B) woven structure; (C) hexagon structure, and (D) hole structure.

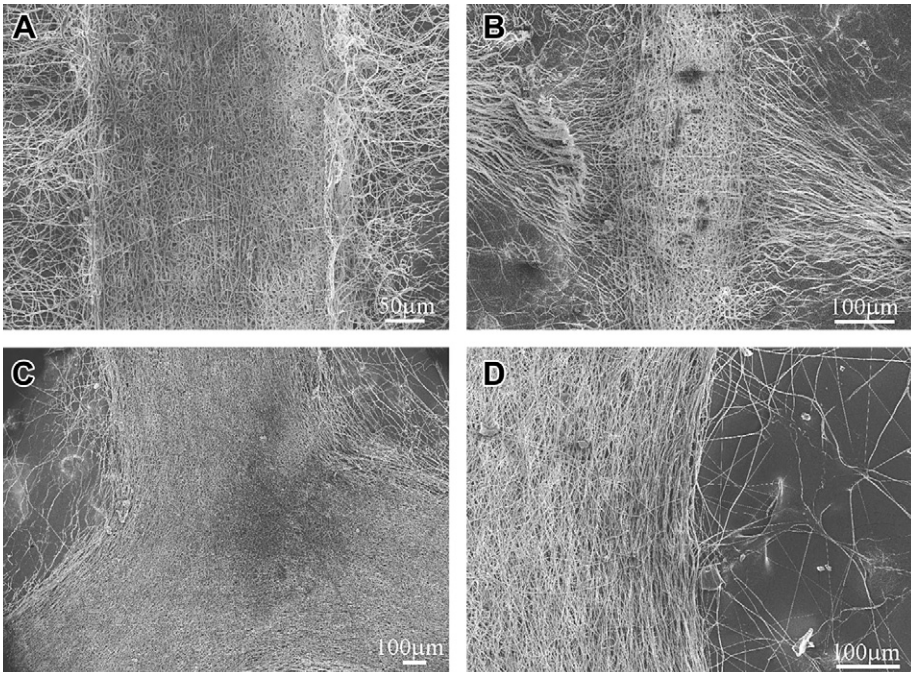

Fig. 4. High-magnification SEM images of electrospun membranes of (A) a parallel line; (B) a crossover point in the woven pattern; (C) a Y-connection in the hexagonal pattern, and (D) the edge of a circular hole.

3. Results and discussion

Digital images of the free-standing electrospun mats resulting from the template-assisted collection process are shown in Fig. 2. The membranes are easy to peel off of the collectors and manipulate. In contrast to randomly assembled electrospun membranes, membranes prepared using template collectors can form well-organized topological structures as evident in the images. The majority of the fibers were deposited onto the electroconductive areas of the collectors, and the overall assembly of the fibers strongly depended on the collector topography. The features on the electrospun membranes were the same shape and had the same dimensions as the collector configurations: parallel and woven lines, hexagons, and circular holes. Some slight distortions apparent in the digital images are due to the fact that the mats do not lie perfectly flat when placed on a paper surface for imaging. Detailed characterizations of the dimensions for each of the patterned membranes are provided in the discussion that follows below.

SEM images of the electrospun membranes in Fig. 3 provide more details on the fiber microstructure. For the collector patterned with parallel wires, the majority of the electrospun fibers directly assembled along the electroconductive lines with a few fibers falling between the lines (Fig. 3(a)). The features in the electrospun membrane are parallel lines with widths of 350 μm and spacing of 1.7 mm, approximately. Fig. 3(b) shows an SEM image of the woven membrane configuration with crossover of the electrospun fibers at points corresponding to intersections of the wire threads in the collector. The assembled fibers form a square-hole configuration with most of the fibers assembled in threads along the electroconductive sidelines of the squares, and a few fibers deposited within the square holes. The threads assembled from the fibers have an average width of 270 μm and the dimensions of the square holes are approximately 670 × 670 μm. For the hexagonal-structured collector, the majority of fibers are deposited along the electroconductive lines of the collector with a few fibers assembling within the hexagonal holes. Fig. 3(c) shows an SEM image of a Y-connection within the electrospun hexagon structure with an angle of 120° between each line. The width of the electrospun lines is approximately 850 μm and the diameter of hexagonal hole is 6.5 mm (Fig. 2(c)). An SEM image of the microstructure of the membrane with circular holes is shown in Fig. 3(d). Almost all the electrospun fibers are assembled onto the electroconductive region and only a few fibers are deposited within the

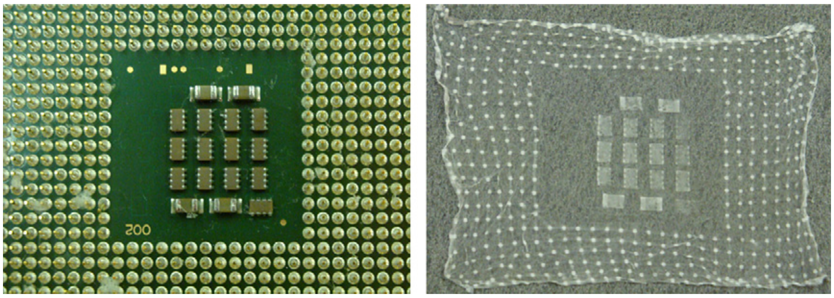

Fig. 5. Digital images of a chip template-collector and the corresponding free-standing electrospun membrane with identical architecture.

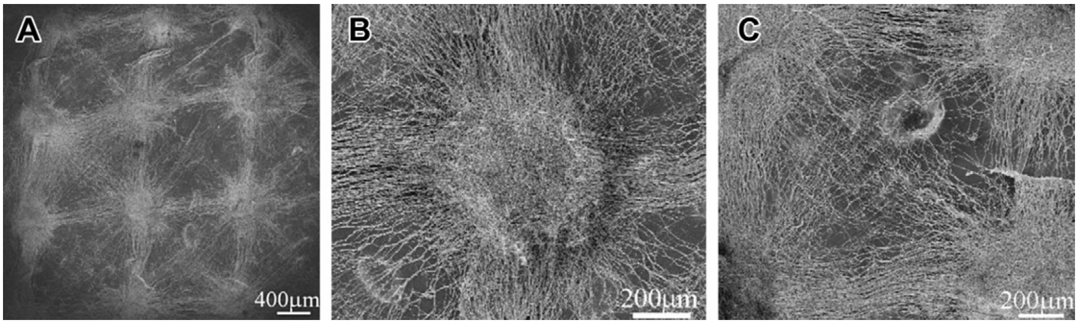

Fig. 6. SEM images of the free-standing membranes prepared using a chip template-collector: (A) electrospun fibers over an array of protrusions; (B) electrospun fibers centered on a protrusion point; (C) electrospun fibers over a square formed by four neighboring protrusions.

circular holes. The diameter of the circular holes is approximately 1.5 mm and the shortest distance between each hole is 1.7 mm.

Fig. 4(a)–(d) are high-magnification SEM images of the free-standing membranes corresponding to the micrographs in Fig. 3 (a)–(d), respectively. These high-magnification SEM images verify that the electrospun fibers primarily assemble over the electroconductive regions of the template collectors. The diameter of a single electrospun PCL fiber is approximately 1.0 μm. Depending on the collector configuration, the assembly and alignment of the electrospun fibers can both be manipulated for a specific structure using the template-assisted electrospinning process. Template-assisted electrospinning is thus capable of

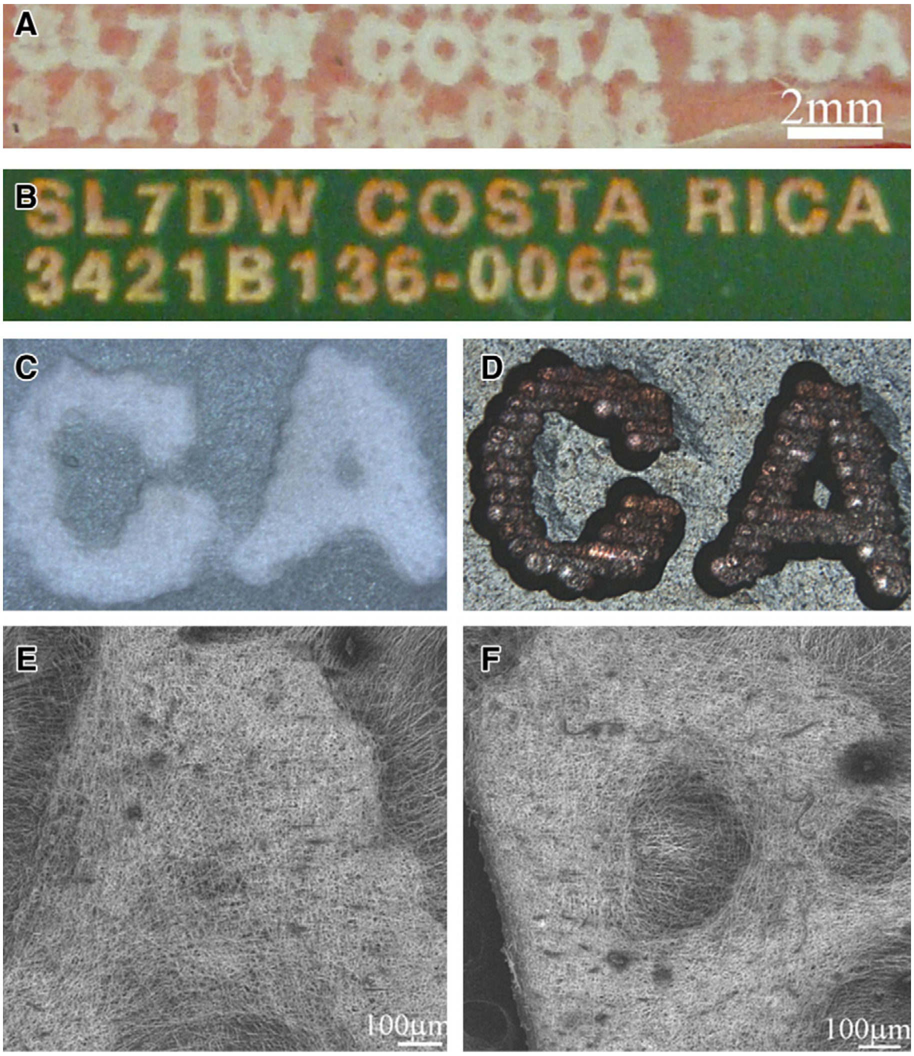

Fig. 7. Digital images of (A) the electrospun membrane with letters and numbers and (B) the corresponding template-collector (C) optical images of the letter “C” and “A” in the electrospun membrane and (D) the corresponding part of the collector. SEM images of letters “A” and “D” in the free-standing electrospun membrane are shown in (E) and (F), respectively.

micro-alignment and macro-assembly of the fibers to create a desired global pattern.

Complex templates can also be utilized, for example one can be designed based on a printed circuit chip. A digital images of the chip template and an electrospun membrane generated using this collector is shown in Fig. 5. The image of the membrane shows the electrospun fibers were homogenously assembled onto the protrusion points of the collector. The majority of fibers were deposited near the electroconductive pins with a spacing of 1.1 mm. Fig. 6 shows SEM images that provide a closer look at the membrane formed using this collector. Fibers were observed on the protrusion points as well as in the spaces between. Specifically, the fibers between protrusions were aligned in vertical and horizontal directions, connecting the pairs of protrusions separated by the shortest distances to generate square configurations (Fig. 6(a)). A few fibers were also observed to align in diagonal directions towards the second closest set of neighboring protrusions. The SEM image in Fig. 6(b) shows the deposition of electrospun fibers centered over a single protrusion, demonstrating the fiber assembly over the protrusion and the surrounding crisscross fiber pattern that is generated by the horizontally, vertically, and diagonally aligned fibers. Fig. 6(c) shows a magnified image of a square formed by four neighboring protrusions. The fibers exhibited a stronger tendency to assemble along the sidelines of the square compared to the diagonal directions. This assembly pattern can be attributed to the heterogeneous electrostatic field generated by the array of conductive protrusions, which produces a stronger attractive force along the sidelines compared to the diagonal directions [23,24]. These experimental results indicate that template-assisted electrospinning can be utilized to manipulate and assemble electrospun fibers into free-standing membranes with specific structures by designing the features of the collectors to produce controlled electrostatic forces.

Fig. 7(a) and (b) show digital images of a template composed of letters and numbers, and the free-standing electrospun membrane produced using this collector. The template-collector consisted of electroconductive alphanumeric characters on an insulating plastic substrate. The dimensions of each character were approximately 1.0 × 1.0 mm. When electrospun PCL fibers were deposited onto the collector, the fibers preferentially assembled over the electroconductive alphanumeric structures due to Coulombic interactions [25,26]. The template-assembled electrospun characters are clearly readable from Fig. 7(a). Close-up optical images of the electrospun letters “C” and “A” show that the most of electrospun fibers accurately assembled to reproduce the letters “C” and “A” on the substrate (Fig. 7(c)) when compared to the features of the copper letters “C” and “A” on the template-collector (Fig. 7(d)). Fig. 7(e) and (f) show SEM images of the letters “A” and “D”. The SEM images confirm that the majority of fibers were concentrated on the characters, but they also reveal that some electrospun fibers were deposited in the gaps between characters due to bending instabilities of the charged fibers. The highest density of electrospun fibers was observed over the patterned characters, and the fiber density in the remaining regions between characters was much lower. This technique is envisioned as a unique and versatile in-situ manufacturing approach to direct the assembly of designed configurations of electrospun fibers onto electronic devices. Although some papers reported selective deposition of electrospun fibers in a smaller scale [27,28], this letter mainly demonstrated the preparation of large-scale, free-standing membranes with fine topological structures and to their potential in macroscale applications, such as tissue engineering and the manufacture of electronic components.

4. Conclusions

In summary, free-standing membranes with various structural configurations were successfully generated with an electrospinning technique using patterned, electroconductive collectors. The patterned collectors acted as templates to direct the deposition and assembly of electrospun fibers. The electrostatic force was a key factor in guiding the charged fibers to the desired locations. The strongest forces were produced by the electroconductive regions of the template, attracting the fibers towards these regions such that the membranes replicate the pattern of the original collector. This work has demonstrated that template-assisted electrospinning is a convenient and effective approach for fabricating free-standing membranes with well-designed topological structures. The approach has potential for directly integrating functional electrospun fibers into electronic components with designed configurations to manufacture novel devices. The capability for large-scale production combined with precise control over structural and material properties make template-assisted electrospinning an attractive tool for micro-manufacturing applications.

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