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Research Article

Preparation of Highly Ordered Fiber Micropatterns by Assembly of Electrospun Nanofiber Segments

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A novel method for fabricating highly ordered fiber micropatterns by assembly of electrospun nanofiber segments was described. Polymethylglutarimide (PMGI) fiber segments with an average length of 3 μm were prepared by combining electrospinning with subsequent sonication treatment. Afterwards, the fiber segments dispersed in water were assembled on Norland optical adhesive (NOA) templates with different microstructural sizes and shapes, allowing formation of spatially uniform nanofibrous micropatterns on flat glass substrate. Regular fiber microarrays were produced when the feature size of NOA template was larger than 30 μm for square and strip geometry. In each microdot, the fiber segments had several layer thicknesses. This new method, which can prepare fiber micropatterns for different materials and microstructures, is suitable for functional device and cell biology applications.

1. Introduction

Electrospinning produces continuous fibers of various natural and synthetic polymer systems, during which a pendent drop of polymer at the nozzle of a spinneret is highly electrified by applying a high voltage between the spinneret and the collector. When the electrostatic repulsion force exerted by the external field overcomes the surface tension of the solution, a fluid jet is ejected out from the spinneret, travelling through air with continuous solvent evaporation. Finally, it is deposited on the collector [1–3]. Electrospun nanofibers have attracted considerable research interest and have been applied in tissue engineering, photonic devices, catalyst supports, composite reinforcements, and so forth [4–9]. Particularly, nanofiber biomaterials, as excellent frameworks, have been extensively investigated to enhance cell adhesion, proliferation, and differentiation because of the porous structure resembling extracellular cell matrix (ECM), easy functionalization, and various components of the fibers [6, 8, 10, 11]. In general, electrospun fibers are randomly deposited on the collector into nonwoven mats. To maximally mimic natural ECM scaffolds, it is of great significance to develop a method for preparing electrospun fibers with more complex and regular structures for biomedical applications.

During the last two decades, there has been remarkable progress in the fabrication of electrospun fibers with different structures [12–15]. They can be collected as uniaxially aligned arrays by using specially designed collectors of different shapes and arrangements such as a pair of split electrodes, a rotating drum and frame, and an apparatus producing focused electric or magnetic fields [16–20]. Furthermore, Blakeney et al. prepared three-dimensional, low-density, uncompressed nanofiber structures by using a grounded spherical dish and an array of needle-like probes as the nanofiber collector, and the resultant fibers were more advantageous to cell infiltration and growth [10].

Additionally, the patterning of electrospun nanofibers into spatially ordered microarrays is quite desirable for being capable of controlling the spatial substrate topography and adhesion as signals to investigate cellular interactions with their surroundings [21–23]. To this end, several methods, including selective deposition of fibers through specialized collectors [24, 25], microcontact printing [26], direct melt writing [27], photolithography [28], and dissolution printing [29], have been used to construct patterned electrospun fibers of various components. Although patterned electrospun nanofibers have been successfully fabricated by these methods, they are limited in versatility, such as requirement

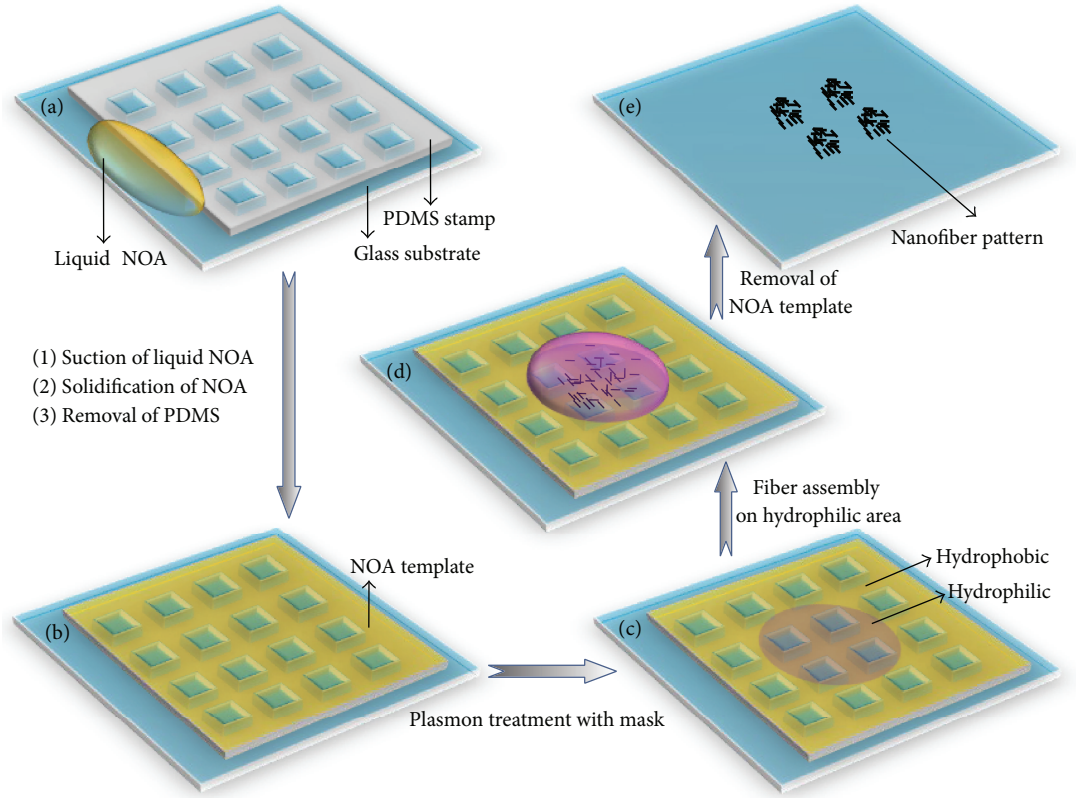


Figure 1: Scheme for the fabrication of nanofibrous micropatterns by assembly of fiber segments: (a) PDMS on glass substrate; (b) NOA template on glass substrate; (c) plasmon-treated NOA template under mask to produce hydrophilic area; (d) water droplet on hydrophilic area; (e) fiber patterns after removal of NOA template.

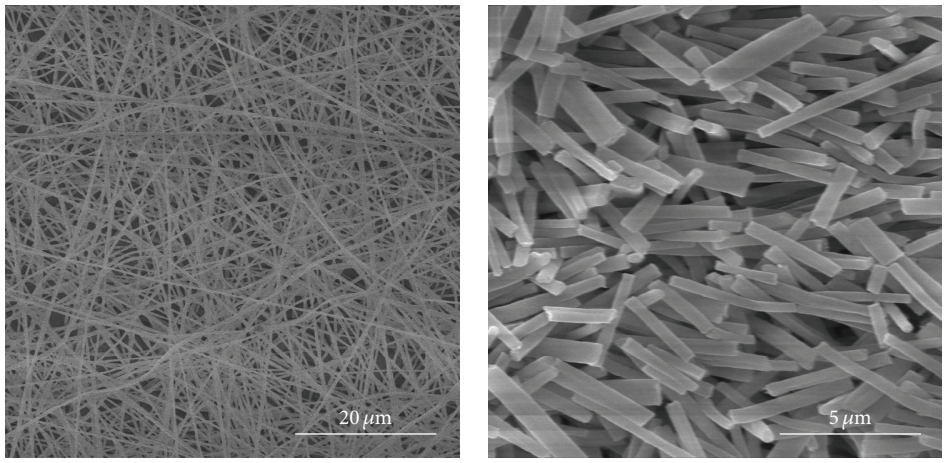
of particular electrode design or complicated setup and involvement of photosensitive polymers or hydrogels. Hence, it is of great benefit to develop a facile technology platform which creates arbitrarily shaped micropatterns of electrospun fibers. In this work, we presented a novel strategy for the production of fiber micropatterns by combining conventional electrospinning with assembly of fiber segments on a featured template. As a result, highly ordered nanofibrous micropatterns with square or strip shape formed on flat glass substrate for potential applications in cell biology and tissue engineering.

2. Materials and Methods

The solution of polymethylglutarimide (PMGI) at 11% in tetrahydrofuran (THF) and cyclopentanone was purchased from MicroChem Inc., Norland optical adhesive (NOA) 81 was produced by Norland Products Inc., and sodium dodecyl sulfate (SDS, ≥97%) and rhodamine 6G (R6G) were purchased from Guoyao Inc. (Shanghai, China). PDMS elastomer (Sylgard 184) was purchased from Dow Corning. The high-voltage supply (DW-P303-1ACF0) was provided by Dongwen Inc. (Tianjin, China).

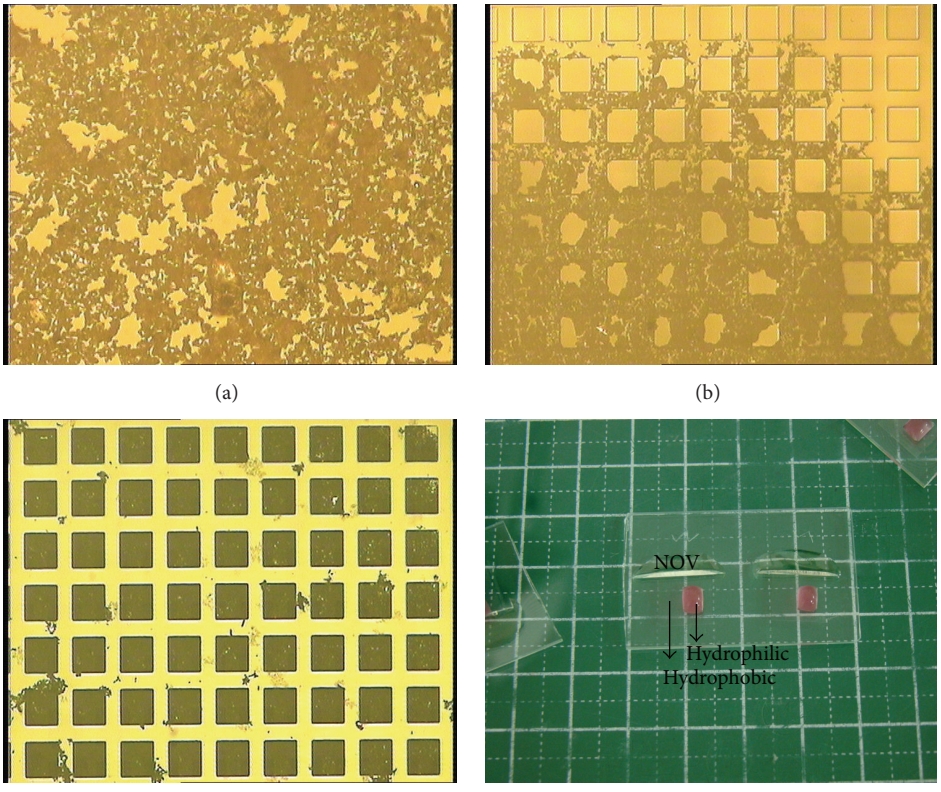
2.1. Formation of Magnetic Nanofiber Segments. Polymethylglutarimide (PMGI) fibers were prepared by electrospinning at room temperature (24°C) at humidity of 40%. Typically, the solution for electrospinning was prepared by dissolving SDS at a concentration of 1.0 mg/mL in PMGI solutions. The polymer solution was loaded into a syringe of 1 mL with a stainless steel needle connected to a high-voltage supply. Electrospinning was performed with a distance to the collector of 10 cm, a voltage of 9.0 kV, and a feeding rate of 10 μL/min. The nanofibers were deposited on a tin foil collector. To facilitate observation of the fibers, fluorescent nanofibers were prepared by electrospinning polymer solution doped with R6G at concentration of 2 mg/mL. To obtain nanofiber segments, the as-spun nanofiber membrane was peeled off from the collector and irradiated under UV light to obtain a hydrophilic surface. Then, the fiber mat was soaked into DI water and sonicated at 40 W for at least 30 min.

2.2. Fabrication of Fiber Segment Patterns. Figure 1 shows the schematic illustration of patterning fiber segments, including formation of NOA template and assembly of fiber segments thereon. The glass substrates were cleaned with piranha solution (H_2SO_4 : 30% H_2O_2 = 7 : 3 v/v) for 30 min, rinsed with copious amounts of water, and dried with N_2. PDMS stamps sized approximately 3 × 3 cm^2 contained symmetric chessboard patterns with 100, 80, 60, 50, 40, 30, and 20 μm wide squares, from which all sides were cut off with a sharp knife to generate open channels. The thus-cut PDMS stamp



(a) (b)

Figure 2: SEM images of as-spun PMGI fibers (a) and fiber segments after sonication for 30 min (b).



(a) (b)

(c) (d)

Figure 3: Optical images of fiber segments assembled on hydrophilic flat glass substrate (a), hydrophobic NOA template (b), and hydrophilic NOA template (c); digital image of fiber segments containing water droplets on hydrophilic NOA template (d).

was placed on the clean glass substrate, on the top of which a force by hand was then applied to ensure close contact between the stamp and the substrate. A drop of NOA 81 solution was then dropped at one end of the open channels of PDMS stamp (Figure 1(a)). After the whole channel was filled with NOA 81 by degassing under vacuum for 5 min, NOA 81 was solidified for 2 min by UV irradiation. Then, the PDMS stamp was carefully peeled off and NOA patterns formed on the glass substrate (Figure 1(b)).

2.3. Assembly of Fiber Segment. The prepared NOA template had a hydrophobic surface [30]. After treatment with

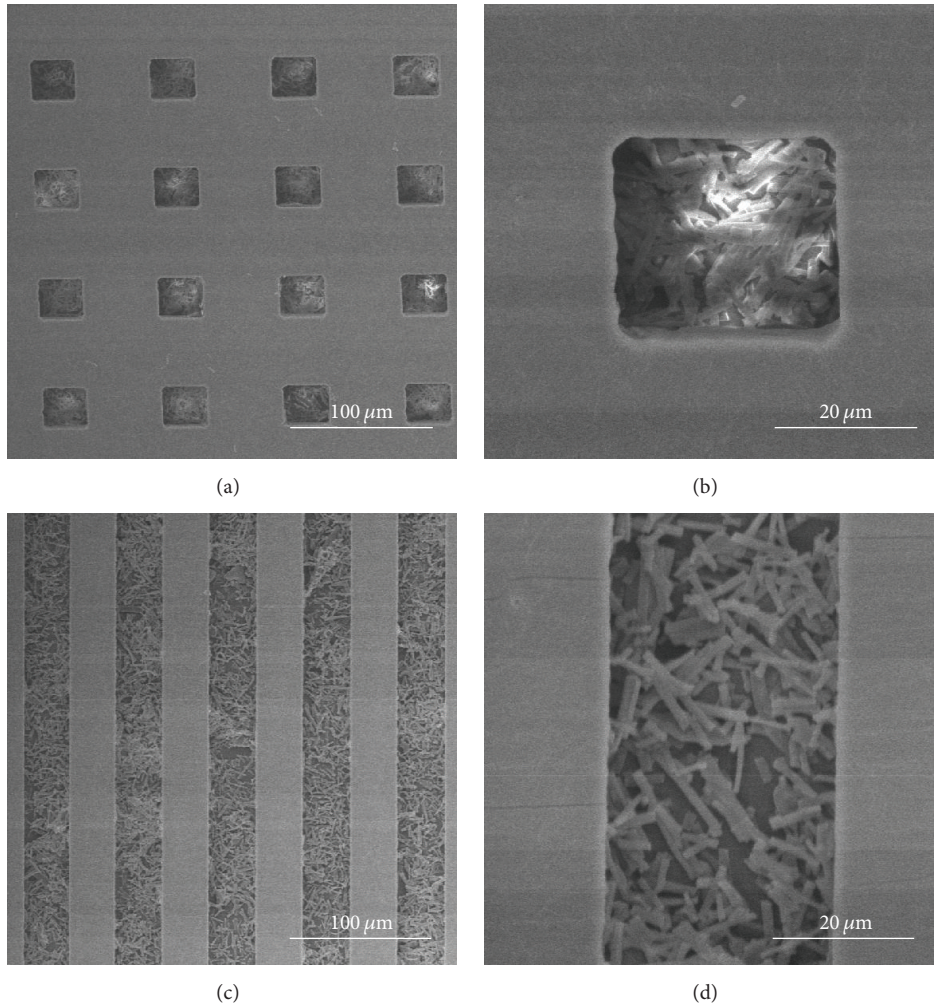


Figure 4: SEM images of the fibers assembled on the square- (a, b) and strip- (c, d) shaped NOA template with feature size of 30 μm, respectively.

plasmon for 5 min under a piece of scotch tape containing an open hole of $1 \times 1\,cm^2$, a $1 \times 1\,cm^2$ hydrophilic zone surrounded by hydrophobic area was generated (Figure 1(c)). Water solution containing fiber segments was sonicated for 10 min before assembly to fully disperse the fiber segments. Afterwards, several drops of water containing fiber segments were quickly dropped on the hydrophilic area and dried overnight in air without disturbances (Figure 1(d)). Finally, the NOA template was removed carefully with tweezers, and fiber micropatterns were fabricated on the glass substrate (Figure 1(e)). The morphologies of the fiber segments and micropatterns were characterized by scanning electron microscopy (SEM, Hitachi S-4800).

3. Results and Discussion

Polymeric fiber micropatterns were fabricated via three processes: (1) formation of nanofiber mats by electrospinning; (2) generation of fiber segments by ultrasonication; (3) assembly of fiber segments into spatial micropatterns. To produce polymeric nanofibers, a commercial solution of 11% PMGI was chosen due to high thermal stability (glass transition temperature Tg: ~190°C) [31]. At a voltage of 9 kV, fibers were ejected from the needle and collected on tin foil. SEM images (Figure 2(a)) show that the as-prepared fiber has uniform morphology, with a typical length of several centimeters and average fiber diameter of 400 nm. Sonication was herein utilized to cut the fiber mats into short fiber segments. To meet the assembly requirement of hole-microstructured NOA template, the length of fiber segments should be minimized. After 30 min of sonication, the fiber segments had a relatively narrow length distribution of around 3 μm (Figure 2(b)). Moreover, this sonication method is simple, safe, and efficient for not destroying the surface morphology of the fiber segments. The resultant fiber segments had small dimensions which were proper for the pattern formation by assembly.

Direct assembly of the fiber segments on flat glass substrate with plasmon-treated hydrophilic wettability as well as on the patterned NOA template with hydrophobic wettability was firstly studied. Fiber segments containing water were

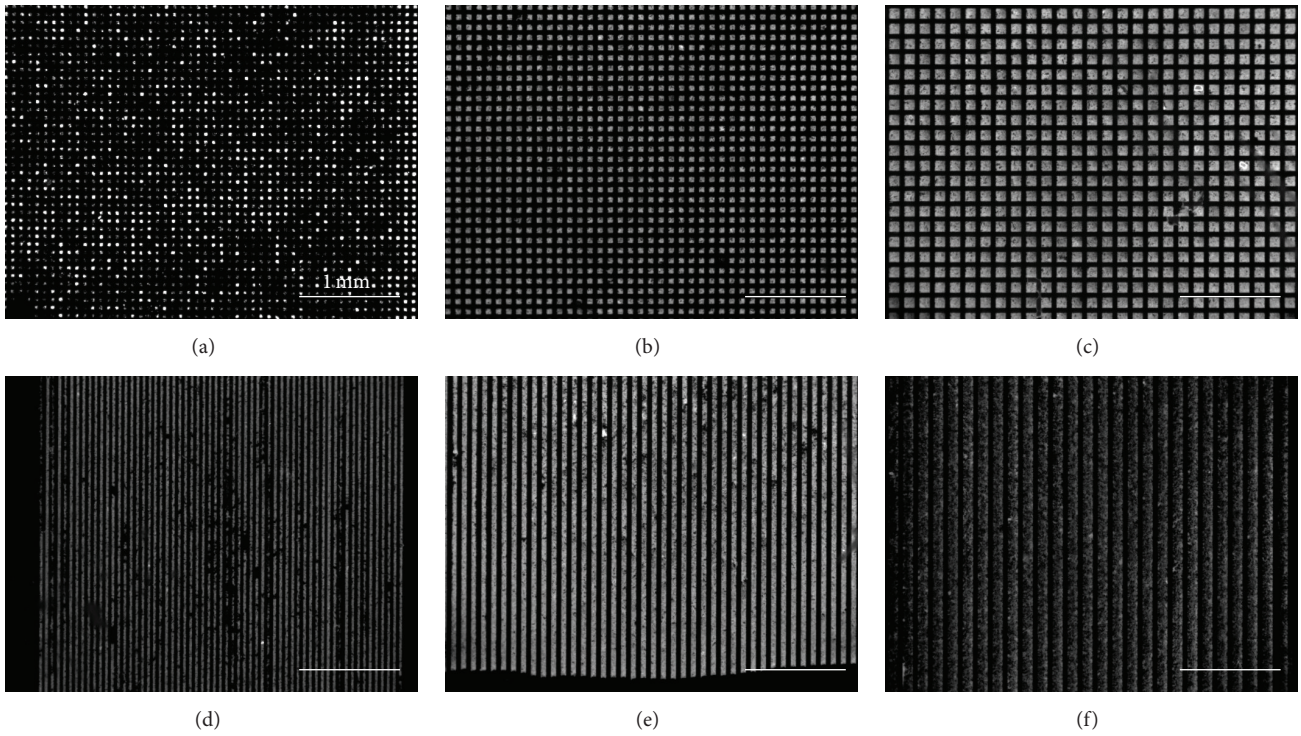


Figure 5: Fluorescent images of the patterned fibers with different feature size on flat glass substrate after removal of NOA template: 30 μm (a, d), 50 μm (b, e), and 100 μm (c, f), respectively. The scale bar is 1 mm.

dropped on the substrate and dried in air. Figure 3(a) shows the optical images of the fiber segments directly assembled on the flat glass substrate. Nearly all the substrate wetted by water was deposited with fiber segments, which can be attributed to the same wettability of the substrate as that of the fiber segment dispersion. Figure 3(b) shows the optical image of the fiber segments assembled on the patterned NOA substrate. Most fiber segments were deposited on NOA template, whereas there were no obvious fibers on the glass squares owing to the wettability difference between the hydrophilic fiber segments and the hydrophobic NOA substrate. Therefore, the fibers were prevented from entering the holes of the NOA template. Figures 3(a) and 3(b) suggest that the fiber segments dispersed in water might be well assembled on the hydrophilic patterned substrate.

Based on the above results, highly regular patterns of fiber segments were obtained by assembly on the hydrophilic patterned NOA substrate with hole arrays. To generate the hydrophilic surface, the NOA template was first treated with plasmon for 5 min under a mask with an open hole, giving a $1 \times 1\,\text{cm}^2$ hydrophilic area surrounded by hydrophobic area thereon (Figure 1(c)). Hydrophilic treatment of the NOA template not only promoted entrance of the fibers into the holes, but also defined the wetted areas for the fiber dispersion. Figure 3(d) is the digital image of the fiber droplet on the plasmon-treated NOA template. As exhibited in Figure 3(d), the red water dispersion is only located on the hydrophilic areas. After drying overnight in air, water was evaporated completely. Figure 3(c) exhibits the optical image of the fiber segments left on the hydrophilic areas on the patterned NOA substrate. There were regular square-shaped patterns with dark color on the substrate, corresponding to the hole pattern arrays on NOA template. Accordingly, most fiber segments had been deposited into the holes during solvent evaporation. A few fiber segments were found on the NOA surface between adjacent holes, which, however, could be readily removed when the NOA template was peeled off.

Assembly of the fiber segments on NOA template was further examined by SEM (Figure 4). By using NOA templates with different geometric figures such as square (Figures 4(a) and 4(b)) and strip (Figures 4(c) and 4(d)) of 30 μm width, the fibers were well deposited into the holes, barely being left on the template surface. Such efficient assembly may be attributed to two reasons. On the one hand, fiber segments were pushed into the template holes by sufficiently strong capillary forces when the liquid dewetted from the bottom surface [32]. On the other hand, the heavy fibers easily fell into the hole because of the height difference between the NOA surface and glass substrate.

The aim of this study was to construct fiber micropatterns on flat substrate for potential bioapplications. Figures 5(a)–5(c) show the fluorescent images of the fiber arrays on flat glass substrate after removal of NOA templates with square feature sizes of 30, 50, and 100 μm, respectively. To facilitate observation, fluorescent fibers were prepared by doping R6G into the PMGI nanofibers. When assembled on the NOA substrates with 50 (Figure 5(b)) and 100 (Figure 5(c)) μm square-shaped templates, each fluorescent microdot

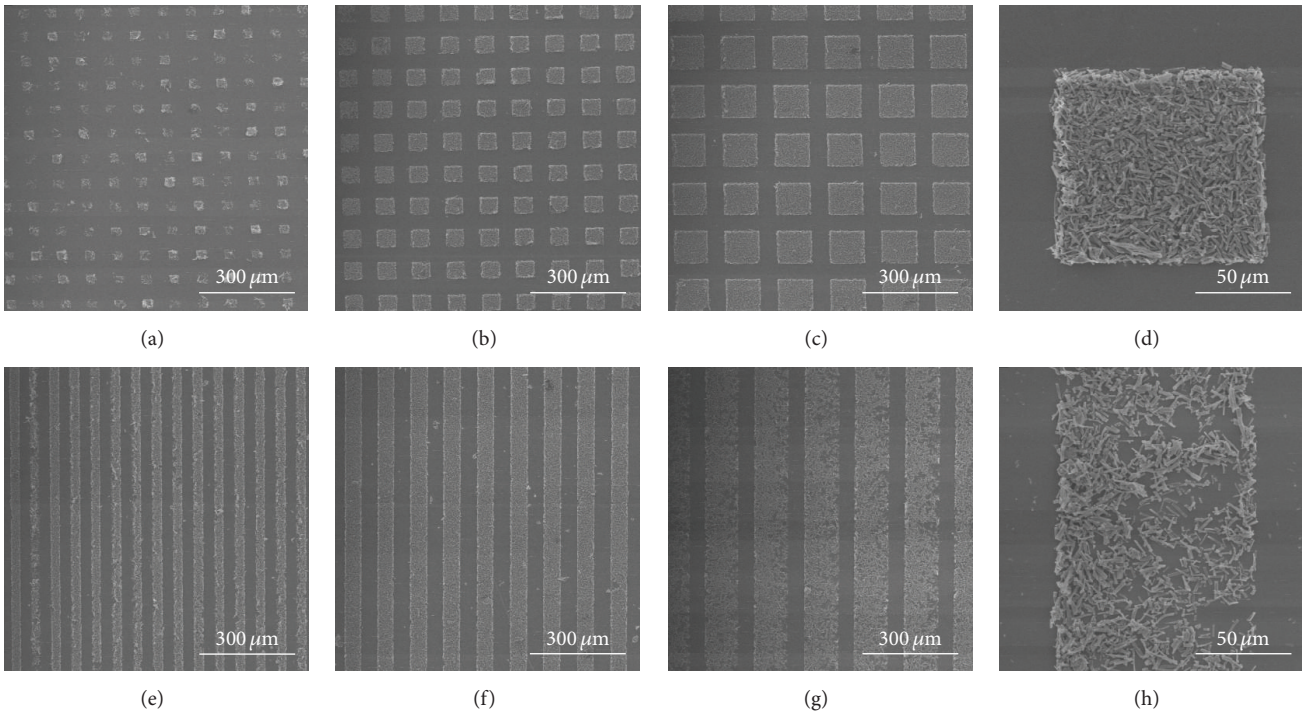


Figure 6: SEM images of the patterned fibers with different feature size on flat glass substrate after removal of NOA template: 30 μm (a, e), 50 μm (b, f), and 100 μm (c, g), respectively. (d) and (h) are the magnified SEM images of (c) and (g), respectively.

remained intact with a regular square shape, suggesting that removal of NOA template hardly affected the fiber pattern. However, edges of the fiber micropatterns assembled on NOA template with a smaller feature size (e.g., 30 μm) were prone to influence by removal of the template, thus losing some fiber segments. In comparison with the assembly on square-structured template, fibers were well retained on the glass substrate after removal of the NOA template with stripe widths from 30 to 100 μm, because the fibers had more contact interface with the hole template compared to that in the strip structure. Given the uniform fluorescent intensity of each microstructure (Figure 5), highly regular and uniform fiber micropatterns were obtained by assembly of fiber segments.

Figure 6 shows the SEM images of the assembled fiber segments on NOA templates with different feature sizes and microstructures. As presented in Figures 6(b) and 6(c), the fiber patterns are extremely regular and uniform for the fiber segments assembled on square templates with feature sizes of 50 and 100 μm. Furthermore, each fiber microdot had the same dimension as that of the hole template. In each microdot, the fiber segments were randomly deposited on the glass substrate with several layer thicknesses (Figure 6(d)). When the size of the hole template was smaller than 30 μm, fiber segments on the glass substrate were easily lost while the NOA template was removed, probably due to their relatively large dimensions (3~5 μm) compared to assembly on the 50 or 100 μm wide hole template. Similarly, this method is also applicable to the preparation of highly ordered fiber micropatterns on the strip templates sized 30, 50, and 100 μm (Figures 6(e)–6(h)). Figures 5 and 6 both indicate that micropatterned fibers with different feature sizes and geometric shapes can be efficiently fabricated by assembling fiber segments on NOA template.

4. Conclusions

In summary, we have developed a new patterning method for producing highly uniform fiber microarrays by assembly of electrospun nanofiber segments. PMGI fiber micropatterns with feature size as small as 30 μm were fabricated on flat glass substrate. This new hierarchical patterning method is simple and versatile, which can be readily extended to pattern other materials. The capability of patterning fibers onto the flat substrate with controlled geometry and dimension opens new avenues to numerous potential applications such as array-based cell culture and microdevice fabrication.

Competing Interests

The authors declare that there are no competing interests.

Acknowledgments

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