

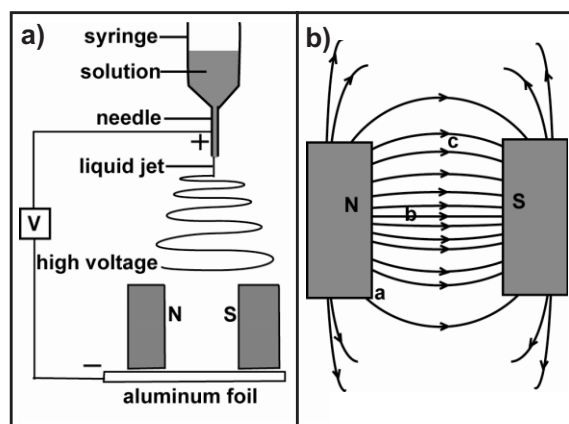
# Fabrication of Aligned Fibrous Arrays by Magnetic Electrospinning\*\*

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This Communication demonstrates a method that generates parallel fibers via electrospinning (ES) magnetic-particle-doped polymers in a magnetic field. ES is a simple method for generating ultrathin fibers with diameters ranging from tens of nanometers to tens of micrometers.<sup>[1–5]</sup> ES possesses several attractive features: comparatively low-cost, relatively high production rate, the ability to generate materials with large surface area-to-volume ratios, and applicability to many types of materials. These features have enabled many applications.<sup>[6–10]</sup> During electrospinning, the fibers deposited on the collector are typically randomly oriented in the form of non-woven mats. It is desirable to generate periodic structures to broaden the applications of ES. For example, in the fabrication of electronic and photonic devices, well-aligned and highly ordered architectures are often required.<sup>[11,12]</sup> For application of fiber-reinforced polymer composites, the alignment of fibers can improve mechanical properties.<sup>[13]</sup> Well-ordered fibers may also be suitable for many applications in tissue engineering.<sup>[8,14]</sup> There have been a few approaches to improving the orderliness of electrospun fibers.<sup>[15–27]</sup> Matthews et al.<sup>[25]</sup> used a rotating mandrel as a ground target to collect fibers. By controlling the rotation speed of the mandrel, they obtained collagen fibers aligned along the axis of rotation. Katta et al.<sup>[16]</sup> employed a macroscopic copper wire-framed rotating drum as the collector, and the electrospun fibers collected on the drum as it rotated were parallel to each other. Theron et al.<sup>[26]</sup> described an electrostatic field-assisted assembly technique using a tapered and grounded wheel-like bobbin to position and align individual nanofibers into paral-

lel arrays. Because the edge of the bobbin was relatively sharp, this technique could not fabricate well-aligned nanofibers over large areas. Li et al.<sup>[15,17]</sup> fabricated parallel arrays made of polymeric and ceramic nanofibers using a collector consisting of two pieces of electrically conductive substrate separated by a gap. To sum up, existing strategies for making parallel electrospun fibers include modifying the collectors and manipulating the electrical field. These methods can fabricate more or less aligned fibers; however, they still have some drawbacks. Modifying the collectors, such as rotating drums, is a time- and energy-consuming method; moreover fibers fabricated by this method are poorly aligned and cannot be conveniently transferred to different types of substrates. Methods based on electrical fields do not seem to achieve the fabrication of aligned fibers over large areas. It is therefore necessary to explore new and more reliable methods that generate well-aligned electrospun polymeric fibers over large areas.

Herein, we report a facile and effective approach to fabricating well-aligned arrays and multilayer grids by a technique called magnetic electrospinning (MES; Scheme 1), where magnetized fibers are stretched into essentially parallel fibers over large areas (more than 5 cm × 5 cm) in a magnetic field. Compared with other reported methods, MES possesses the following advantages: a) The apparatus is simple and requires only adding two magnets to a conventional setup; b) The



**Scheme 1.** a) Illustration of the apparatus for magnetic electrospinning (MES) to generate aligned fibers. The key component of the system is a magnetic field generated by two parallel-positioned permanent magnets. b) Calculated magnetic field strength vectors in the region between the two magnets [28] (top view). The arrows denote the direction of the magnetic field lines. The representative magnetic field strength of *a*, *b*, and *c* is 120, 32, and 25 mT, respectively.

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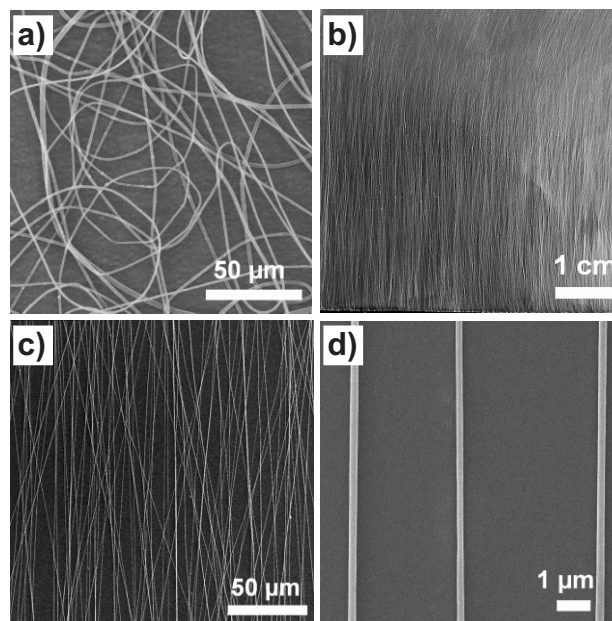
magnetic field can be manipulated accurately; c) The resultant nanofibrous arrays can be transferred onto any substrate from any angles with full retention of their structures; an advantage that can be further used to construct more complicated structures; d) The area of the aligned fibers is large compared to fibers generated with other methods.

In MES, the polymer solution is magnetized by the addition of a small amount (less than 0.5 wt %) of magnetic nanoparticles. We spin the solution into fibers in the presence of a magnetic field generated by two parallel-positioned permanent magnets (Scheme 1a). The magnetic field stretches the fibers across the gap to form a parallel array as they land on the magnets. An aluminum foil placed between the bottoms of the magnets acts as the cathode. The length of the gap between the magnets can be varied from several millimeters to several centimeters, which determines the width of the resultant arrays. During MES, bunches of fibers fall down, the segments of the fibers close to the magnets are attracted to the surface of the magnets, finally the fibers land on the two magnets and suspend over the gap. The resulting fibers can be transferred onto the surface of substrates such as aluminum foils and glass slides.

The polymer used was poly(vinyl alcohol) (PVA). It was dissolved in distilled water at a concentration of 8 wt %.  $\text{Fe}_3\text{O}_4$  nanoparticles with an average diameter of 30 nm were dispersed ultrasonically in the PVA solution for 24 h. Since the nanoparticles could not all disperse in the polymeric solution, we measured the content of  $\text{Fe}_3\text{O}_4$  in the electrospun fibers to be 0.22 wt %, using thermogravimetric analysis (TGA, Perkin–Elmer). Here, the height of the magnets was 6.5 cm, and we defined the vertical distance between the needle tip and the top surface of the magnets as the working distance (WD). During MES, a voltage of 15 kV was applied and the WD was 10 cm. The area of the fibrous woven arrays was 5 cm  $\times$  5 cm (Fig. 1b). We used scanning electron microscopy (SEM) to image the details of these fibers (Fig. 1c and d). Samples for analysis by SEM were collected on an aluminum foil, and then dried and demagnetized in air for two days, and finally sputtered with gold for 60 s (resulting in a coating of about 10 nm). Images from both a digital camera and SEM indicated that MES can produce parallel fibrous arrays.

We speculate the mechanism for the formation of parallel fibers by MES to be the following: A fiber containing magnetic particles can be considered as a thread charged with magnetic dots connected through a viscoelastic medium. As depicted in Scheme 1b, there are many parallel magnetic field lines between the two parallel-positioned magnets running from the N to S poles.<sup>[28]</sup> Empirically, small magnetic particles tend to form lines that delineate the magnetic field. We believe that this tendency allows the fibers doped with magnetic nanoparticles to also delineate the magnetic field, which is essentially a group of parallel lines between these two magnets.

To validate our hypothesis that the magnetic field was indeed responsible for the alignment of the nanoparticle-doped polymeric fibers, we carried out several additional experiments. In one experiment, the magnets were replaced by two

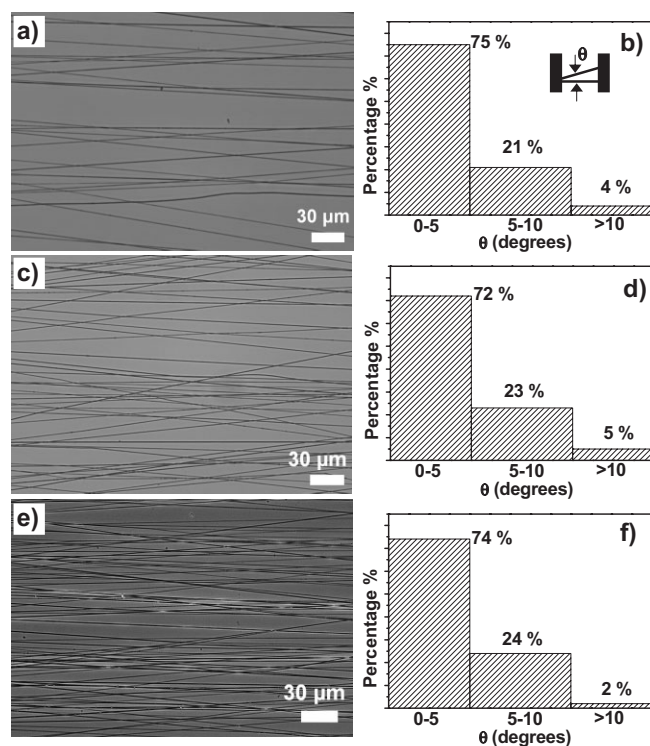


**Figure 1.** a) A typical image of disorderly mats made of PVA fibers via conventional electrospinning. b–d) Images of arrays of PVA fibers fabricated via magnetic electrospinning. b) An image collected by a digital camera. c,d) Scanning electron microscopy (SEM) images of the aligned fibers.

plastic plates, so that the magnetized solution was electrospun without a magnetic field. The fibers landed on the aluminum foil, or the plastic plates, or between the foil and a plate, but they could not suspend over the gap between the plates, thus, resulting in nonwoven mats (similar to Fig. 1a). In the second experiment, we prepared the polymeric solution without adding any magnetic nanoparticles, but the nonmagnetized solution was electrospun in the magnetic field. The resulting fibers were not aligned. The third experiment was to spin the magnetized solution in a magnetic field, but the width of the gap was too wide (e.g., 10 cm), so that the fibers could not suspend over the magnets when they landed. The fibers assembled on the aluminum foil, resulting in a disorderly structure. The fourth was to electrospin the magnetized solution in a very strong magnetic field (about 500 mT); we observed that the magnetized fibers only deposited on the magnets because of the excessive magnetic force. Therefore, an appropriate magnetic field, suitable gap width between the two magnets, and the magnetized polymeric solution are all key factors to the successful fabrication of well-aligned fibrous arrays by MES. MES is thus fundamentally different from all previously reported methods in preparing aligned fibers by electrospinning. For example, some researchers aligned fibers by using two pieces of conductive substrates as collectors,<sup>[15]</sup> in this case, the driving force was the electrostatic interaction. The magnets we used were insulators, being made of a ferromagnetic oxide mineral. These experiments, therefore, confirm our hypothesis that the magnetic field is the real driving force to induce the fibers to align into parallel arrays.

The experimental conditions, such as relative humidity, temperature, concentration of the solution, and the electrical potential, should be carefully adjusted to prepare ordered arrays of fibers. When the temperature was too low or the relative humidity too high, the velocity of solvent evaporation became slow. The resulting fibers tended to be too heavy to suspend over the magnets and fell onto the aluminum foil, in a disorderly manner. Dilute solutions or high electrical potentials generally led to thin fibers; but when the fibers were too thin, they would break because their low mechanical strength could not sustain the weight of the fibers themselves.

We quantified the morphology of the fibers made with different processing times and voltage-to-distance ratios to evaluate the quality of the fibers, such as the alignment and the diameter. We used optical microscopy (OM) to observe the morphology of fibers (Fig. 2). Here we employed the angles ( $\theta$ ) between the long axes of the fibers and their expected direction (parallel to the vectors of the magnetic field) as a parameter to quantify the alignment (Fig. 2b, inset). From these images and the corresponding statistical analysis on alignment, we conclude that most fibers aligned in the desired direction (perpendicular to the magnets; more than 95% of the fibers are within  $10^\circ$  of this direction). The density of the fibers increased with the spinning time, but the degree of the alignment was essentially the same as the spinning time in-

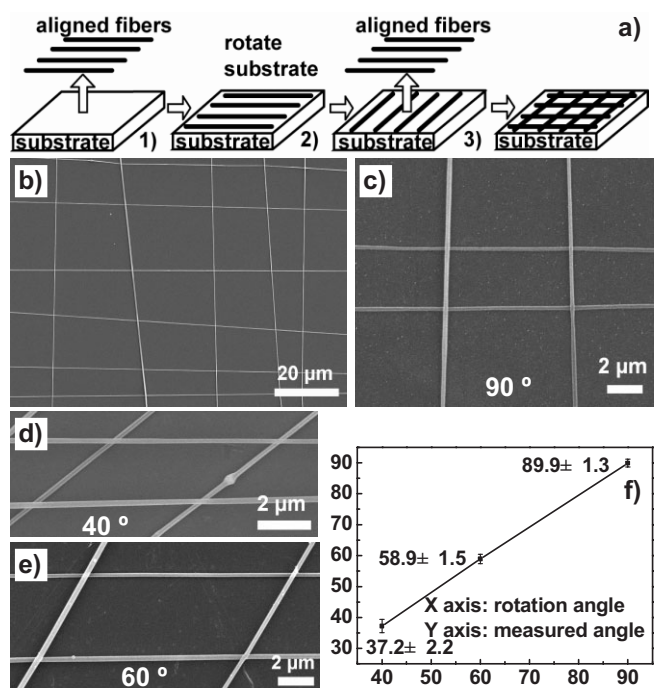


**Figure 2.** a,c,e) Typical optical micrographs of PVA fibers on glass slides with different collection times: 2, 4, and 5 min, respectively. b,d,f) Corresponding distributions of the angle ( $\theta$ ) between the long axis of the fibers and their expected direction. The angles were measured on an Image-Pro Plus instrument. The results came from measurements on more than 100 fibers.

creased. Furthermore, we fabricated PVA fibers with different diameters by changing the voltages applied. We chose a WD of 10 cm and varied the electrical potential from 10, 14, to 18 kV; thus, the different voltage–distance ratios were 1.0, 1.4, and  $1.8 \text{ kV cm}^{-1}$ , respectively. The diameters of the corresponding fibers were  $360 \pm 12$ ,  $250 \pm 9$ , and  $150 \pm 9$  nm, respectively.

MES of aligned fibers is also applicable to other polymers, such as polystyrene (PS, Aldrich, average molecular weight of 230 000). We dissolved PS in dimethylformamide (DMF) at 20 wt %, then mixed the solution with  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles, ultrasonically dispersed the mixture for 24 h, and obtained a magnetized solution containing 0.46 wt %  $\text{Fe}_3\text{O}_4$ . We applied a voltage of 25 kV and WD of 15 cm for MES. Under these conditions, we obtained aligned arrays of PS fibers.

As the resultant fibers can be transferred onto substrates from different angles, we can employ MES to build structures with greater complexity than just parallel lines. For example, stacking arrays of fibers allows the generation of grids (Fig. 3a). After collecting the first layer on the substrate, we rotated the substrate to collect a second layer in a different direction. Figure 3b and c show SEM images of the rectangular patterns formed via this method with a rotation angle of  $90^\circ$ . Other rotation angles produce grids of parallelograms (Fig. 3d–e). In these cases, the measured angles between the



**Figure 3.** a) The strategy for the formation of multilayered structures: 1) collection of the first layer; 2) rotation of the substrate; 3) collection of the second layer; 4) formation of multilayered grids. b–e) SEM images of the two-layer grids with different rotation angles: b,c)  $90^\circ$ , d)  $40^\circ$ , e)  $60^\circ$ . f) The plot of measured angle versus rotation angle. The angles were measured with an Image-Pro Plus instrument.

fibers in the first layer and the second layer are in agreement with the corresponding rotation angles.

In order to quantitatively examine the height and three-dimensional profiles of the structures formed by MES, we used atomic force microscopy (AFM) in the tapping mode to image the topography of a two-layered grid formed by MES (Fig. 4a and b). The three-dimensional images showed the spatial profile of the grids made of aligned fibers. We generated a height profile of the two-layered grid along a straight line across the nanofibers (Fig. 4c). The height of the fibers in the first layer measured by AFM (196 nm and 197 nm) is comparable with the width obtained from the SEM image (195 nm). The fibers in the second layer stacked on the first layer; therefore, the measured height is larger than that of the fibers in the first layer.

In conclusion, we have demonstrated a facile and effective method for the generation of well-aligned polymeric micro- and nanofibers over large areas. This method involves a polymeric solution magnetized with small amounts (<0.5 wt %) of magnetic nanoparticles and carrying out the spinning process in a magnetic field. The magnetic field drives the magnetized electrospun fibers to align in a parallel fashion along the magnetic field lines. The resulting fibers form essentially parallel arrays. This method also allows the construction of structures based on parallel arrays, such as grids. We believe that other polymers and polymer–ceramics composites could be fabricated into ordered structures via MES.<sup>[4,29,30]</sup> The embedded magnetic nanoparticles do not affect the morphology of the fi-

bers. Because of the low quantity of magnetic nanoparticles used, we suspect that they do not impact the properties of the fibers for most applications. The aligned fibers can lead to anisotropic properties such as unique electrical,<sup>[31,32]</sup> optical,<sup>[33,34]</sup> wetting,<sup>[35–38]</sup> and mechanical<sup>[39–42]</sup> performances; therefore, the ability to generate periodic, ordered structures easily by MES may broaden the applications of ES, such as in electronic and photonic devices, polymer composites, and tissue engineering. Repeated patterns of fibers are also useful for some applications derived from soft lithography.<sup>[43,44]</sup>

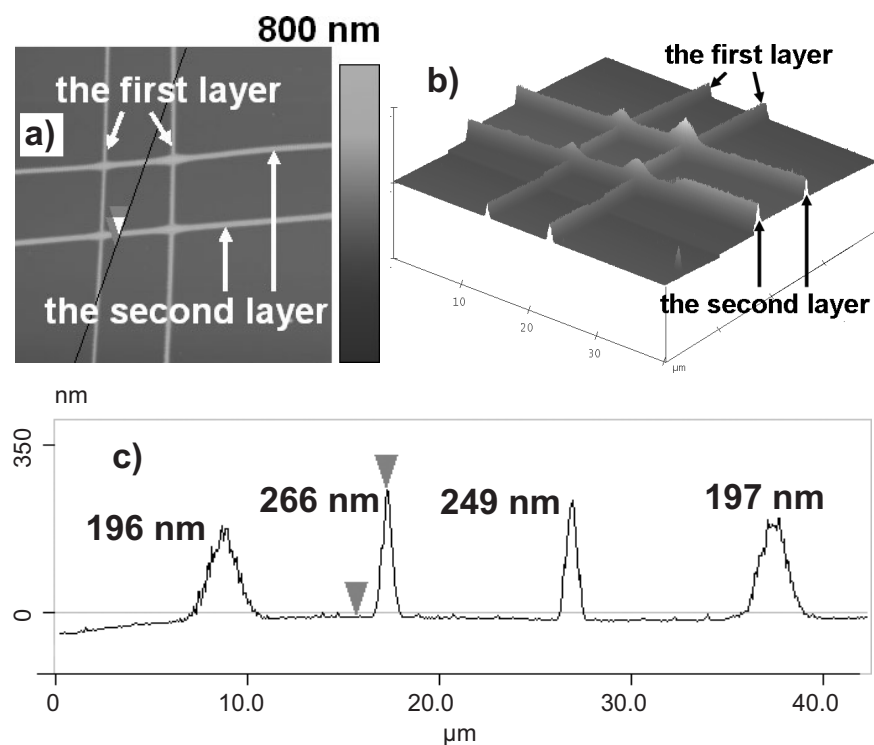
### Experimental

**Magnetic Electrospinning (MES):** The setup for electrospinning is essentially the same as the conventional configuration except for the use of two magnets positioned at the sides of the aluminum foil. The solution was driven from the syringe at a constant rate by a syringe pump. The fibers were electrospun at appropriate voltages and collection distances for different polymers using a high-voltage DC power supply (Spellman High Voltage Electronics Corporation). The spun fibers were suspended between the two magnets. After the electrospinning we used aluminum foils or glass slides as substrates to collect the fibers.

**Morphology Analysis:** We used optical microscopy (OM, Leica DMI6000B), field-emission scanning electron microscopy (SEM, Hitachi S4800) and atomic force microscopy (AFM, DI D3100, tapping mode) to study the morphology of the fibers. Fibers for SEM were collected on an aluminum foil, and then dried and demagnetized in air for two days, and sputter-coated with Au for 60 s (resulting in a gold coating of about 10 nm) to reduce charging effects. SEM was operated at an accelerating voltage of 10 kV. Fibers for OM were deposited on glass slides and the images were collected under bright-field conditions.

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**Figure 4.** AFM images of grids made of aligned fibers. a) An image, along with a dark line showing the position of the nanofiber cross-sectional profile analysis in (b). b) The corresponding three-dimensional image. c) A height profile across the grid of (a).

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