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# Fabrication of various micro/nano structures by modified near-field electrospinning

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The modified near-field electrospinning (NFES) and the conventional NFES have been compared to demonstrate the viability of direct-writing micro/nano structures from PVDF solution systems. The modified NFES shows good capability in writing various orderly micro/nano patterns, such as straight and continuous lines, parallel lines, arc lines, and beads-on-string structures, whereas the conventional NFES is difficult to give a continuous writing process. Besides, the modified NFES also allows a lower electric field due to the jet initiated in a mechanical way. By finely tuning the key parameters during the modified NFES process, such as the solution property, speed of the movable collector, and the distance between the spinneret and the collector, it is likely to construct complex patterns as required on rigid or flexible substrates for a myriad of applications.  [http://dx.doi.org/10.1063/1.4901879]

## I. INTRODUCTION

Electrohydrodynamic printing (EHDP) has attracted an increasing interest due to its low cost, convenient operation and high precision, and the ability of direct-writing different micro/nano structures on different substrates for flexible electronic devices.[1] In 2006, Sun et al. have developed a near-field electrospinning (NFES) technique by shortening the electrode-to-collector distance between 500 µm and 3 mm, where a tungsten electrode with tip diameter of 25 µm was used to construct polyethylene oxide (PEO) nanofibers.[2] Since then, a great deal of efforts has been made for higher precision, larger area deposition, and direct-writing more functional materials, etc. Through fabricating a finer nozzle of glass microcapillary, Rogers et al. have printed complex dot-matrix patterns from an aqueous ink of a blend of poly(3,4-ethylenedioxythiophene) and poly(styrenesulphonate) (PEDOT/PSS).[3] Chang et al. utilized a tungsten probe tip to mechanically draw a single fiber from the droplet to initiate the continuous NFES process, where they constructed complex PEO nanofiber patterns such as circular shape and grid arrays on large and flat areas.[4] Until recently, NFES has been gradually applied to write well-aligned $TiO_2$ nanofibers,[5] aligned sugar-polycarprolactone (PCL) core-shell fibers,[6] light-emitting conjugated polymer nanofibers of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV),[7] and piezoelectric polyvinylidene fluoride (PVDF) nanofibers,[8] etc.

Although much progress has been made, there are no further publications by other groups who have reported PVDF fibers by the NFES technique. The reason may be attributed to its tough solubility in conventional solvents, as reported by Bottino et al. that PVDF is a non-water-solvable polymer, only partly dissolved in a very few highly polar solvents at room temperature.[9] On the other hand, there are very few studies on the Beads-on-String (B-S) structure produced by the NFES.[10] It has been

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reported that luminescent PEO and poly(methyl methacrylate) (PMMA) fibers with “beads on a string” morphology have potentials in photonic applications.[11] Moreover, the too short distance (500 µm) between the spinneret and the collector is liable to cause corona discharge although seldom reported in far-field electrospinning (FFES). Nevertheless, at present we have successfully direct-written the orderly micro/nano patterns, such as intersecting perpendicular lines, arc lines and beads-on-string structure by the modified NFES. Key parameters, such as PVDF solution concentration, speed of the movable collector, and the need tip-to-substrate distance are investigated.

## II. EXPERIMENTAL

Based on our previous studies,[12,13] PVDF ($M_w$~534, 000, Aldrich) solutions of 12 wt% and 8 wt% with N-Methyl pyrrolidone (NMP) and acetone volume ratio ($V_{NMP}/V_{acetone}$) of 6/4 were prepared for both conventional NFES and modified NFES experiments. Briefly, PVDF powders were dissolved in the mixed solvents ($V_{NMP}/V_{acetone}$ = 6/4) with continuous stirring the mixture at 50 °C for a few hours in a parafilm-sealed frosted glass bottle until the solution became transparent. Before the NFES process, the polymer solution was degassed to remove bubbles. In the conventional NFES, an acupuncture needle tip was poked inside the polymer solution meniscus and drew some amounts of the solution on the tip. A high voltage was immediately applied on the tip to eject a polymer jet from the tip. The schematic of this conventional NFES was illustrated in Fig. 1(A). As for the modified NFES, the acupuncture needle tip was utilized to mechanically draw a polymer jet from the charged droplet to initiate the electrospinning process, as shown in Figs. 2(A)-2(C). Normally, a movable collector was used to collect the deposited fibers and the needle tip-to-collector distance was varied between 1 and 5 mm, and the applied voltage was between 1 and 2.5 kV. All experiments were performed at room temperature with relative humidity between 55 and 60%.

A commercial software of Ansys was introduced to analyze the distribution of electric field between the tip and the collector. The jet formation and its motion were recorded under a CCD camera (SONY SSC-DC80 resolution 768×494). The NFES micro/nano patterns were examined by a scanning electron microscope (SEM, LEO 1530, LEO) and a three-dimensional optical microscopy (OM, XL30, Philips). Specifically, the fiber diameter was measured from SEM images using an Image J software.

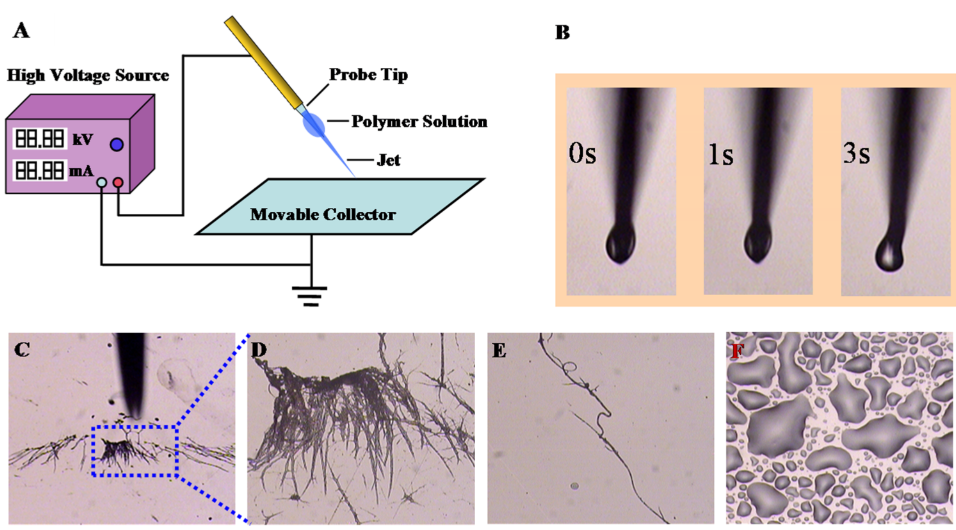


FIG. 1. (A) Schematics of the conventional NFES; (B) variation of the polymer solution on the acupuncture needle tip after applying a low electric bias (0.8 kV); (C-F) optical photos of the NFES samples under different concentrations of 12 wt% for (C, D, E) and 8 wt% for (F), and movable collector with a speed of 0 and 15 mm/s for (C, D, F) and (E), respectively. The $V_{NMP}/V_{acetone}$, the applied voltage, and the tip-to-collector distance are 6/4, 1.8 kV, and 5 mm, respectively.

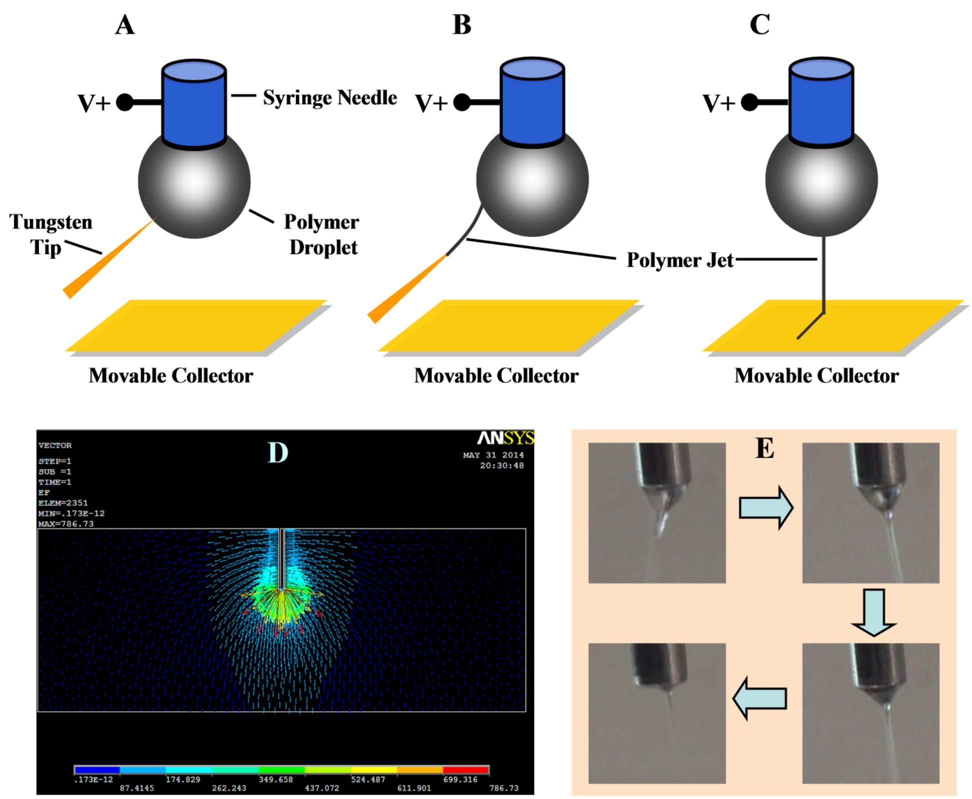


FIG. 2. Schematics of modified NFES- (A) an acupuncture needle tip inserting into polymer droplet, (B) the tip moving off the droplet with polymer jet, and (C) continuous direct writing of the jet; (D) electric field distribution around the needle tip in the NFES process; (E) snapshots of variation of the jet after moving off the acupuncture needle tip.

## III. RESULTS AND DISCUSSION

In the conventional NFES process, the liquid polymer solution is supplied in a manner similar to that of a dip pen, such that the NFES could be terminated at any time provided that the very limited solution on the tip was exhausted (or solidified). When the applied electric field is below a critical value (where electrostatic forces overcome the surface tension forces is required to induce a polymer jet from the tip of Taylor cone), the NFES can not be imitated, as shown in Fig. 1(B), where a low electric bias (0.8 kV) was applied on the tip. It can be seen that the PVDF solution (12 wt%, $V_{NMP}/V_{acetone}$ = 6/4) droplet suspended onto the acupuncture needle tip was deformed and solidified after a few seconds due to the synergistic effect from evaporation of the solvent and electrification of the solution. By increasing the voltage up to 1.8 kV, the electrified polymer jet can be ejected, but the produced fibers are discontinuously distributed on the static collector (Figs. 1(C)-1(D)), which may be attributed to the insufficient solution around the tip failing to keep a continuous NFES process. Although moving the collector at a speed of 15 mm/s can promote the stretching process of the jets, the resulting fibers are not smooth and show many branches (Fig. 1(E)). On the other hand, when a lower concentration (8 wt%) solution was used, an electrospray process was taking place instead, resulting in many small droplets deposited on the collector (Fig. 1(F)).

Therefore, the conventional NFES is not suitable to direct-write PVDF fibers, although it can be utilized to write polyethylene oxide (PEO) nanofibers.[2] In this regard, a modification of the conventional NFES should be performed to achieve a continuous NFES process for PVDF. Hence, the following paragraphs are mainly centering on the modified NFES and the direct-written micro/nano polymer patterns.

The process of modified NFES can be easily known from Figs. 2(A)-2(C), which has been briefly depicted in Experimental part. It should be noted that the needle tip-to-collector distance is much larger than that required in the conventional NFES but no more than 10 mm, as reported that the straight segment of the jet in conventional far-field electrospinning can be extended for about 1 cm above the top of the Taylor cone.[14] It is also of importance that once the acupuncture needle tip successfully draws a polymer jet from the droplet, the high voltage is immediately applied and maintained for the whole electrospining process. A vivid variation of the jet after moving off the acupuncture needle tip can be observed in Fig. 2(E). Since the tip is poked into the left side of the droplet, the jet is ejected in the direction of mechanical drawing (left top in Fig. 2(E)), gradually shifts into the center, and then becomes thinner and stable focusing onto the collector. The main reason for this jet evolvement may be highly related to the centralized electric field between the tip and the collector, as shown in Fig. 2(D). Therefore, this modified NFES is hopeful to direct-write the very long and continuous straight line and other orderly patterns for various micro/nano devices.

In order to test the feasibility of the modified NFES, 12 wt% PVDF solution with $V_{NMP}/V_{acetone} = 6/4$ was experimented and movable substrates with different speeds were used to collect the samples, whose microphotos are shown in Fig. 3. Three key observations are found in this figure. First, the substrates utilizing semi-conducting silicon chip and conducting tin foil are favorable to get aligned fibers (Figs. 3(A)-3(B)), whereas using insulating PET sheet as substrate the wavy fibers are normally obtained (Fig. 3(C)). When the collector is grounded, the conducting and semi-conducting substrates can effectively carry charges off the fibers; however, the fibers collected on the insulating substrate retain charges on themselves, which distort the alignment of the incoming fibers. Second, the substrate moving at a higher speed can remarkably reduce the fiber diameter. It is apparent that the substrate movement will cause post-stretching of the flying jets more or less. Third, the modified NFES process is highly repeatable to direct-write parallel lines, as indicated by Figs. 3(A)-3(B). Within the current experiments, it is hopeful to get aligned submicron or nanoscale fibers by finely tuning the operating parameters.

To further demonstrate its flexibility, the modified NFES was utilized to direct-write different micro/nano patterns on the grounded silicon chip. Fig. 4(A) shows intersecting perpendicular lines constructed using an $x$-$y$ stage (GXY1515GT4, Googol Tech., China) to control the substrate movement. Further by controlling the motion stage, the parallel arc lines can be also obtained, as shown in Fig. 4(B). Besides, straight lines are easily written over the gap of two silicon chips, as displayed in Fig. 4(C) (enlarged picture inset). In the above experiments, PVDF solution of 12 wt%, $V_{NMP}/V_{acetone} = 6/4$, was used. However, when solution of a lower concentration (8 wt%) was experimented, the regular beads-on-string structures which consist of droplets and filaments were generated, as shown in Figs. 4(D)-4(F). As can be known from Figs. 4(E)-4(F), the modified NFES is capable to reproduce the close beads-on-string structures, which shows great potentials in drug delivery system.[15]

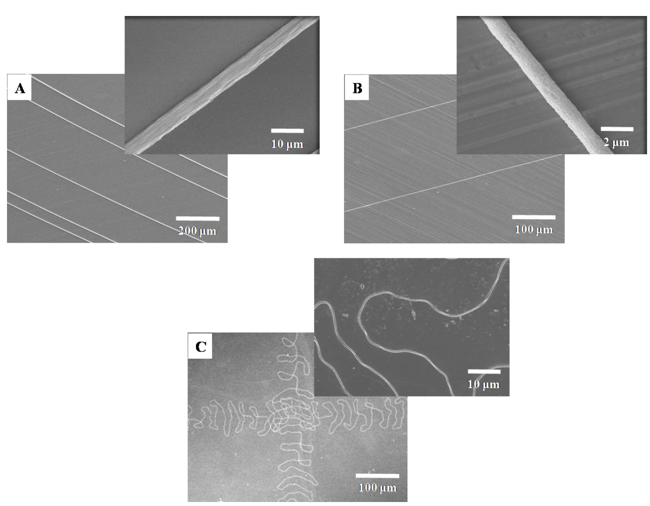


FIG. 3. SEM images of the fibers produced by the modified NFES deposited on different substrates with different speeds: (A) silicon chip moving at 50 mm/s; (B) Tin foil moving at 150 mm/s; (C) PET sheet moving at 80 mm/s. Experimental conditions: PVDF solution of 12 wt%, $V_{NMP}/V_{acetone} = 6/4$, applied voltage at 1.2 kV, flow rate at 80 µL/h, tip-to-collector distance at 5 mm.

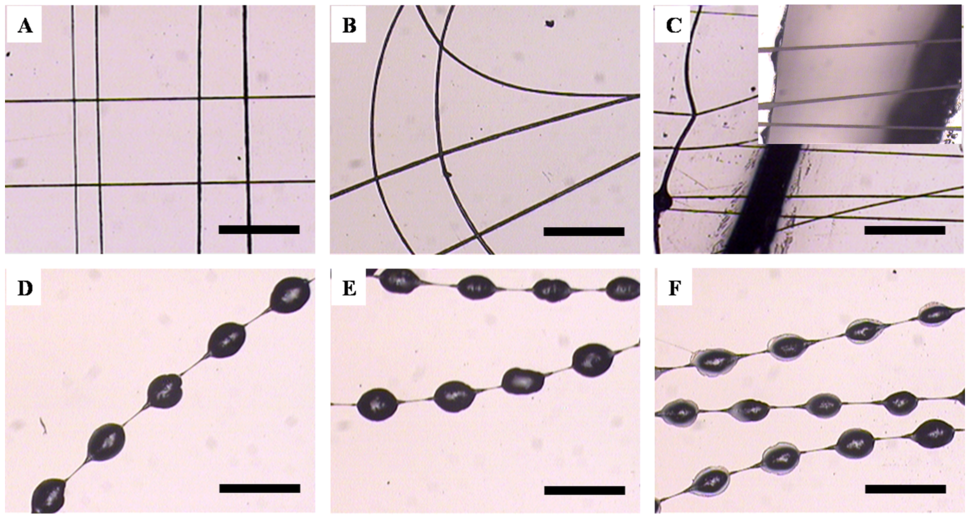


FIG. 4. Optical photos of micro/nano patterns constructed by the modified NFES: (A) intersecting perpendicular lines; (B) parallel arc lines; (C) straight lines crossing over the gap of two substrates (enlarged inset); (D-F) beads-on-string structures which consist of droplets and filaments. The applied voltage, the flow rate, and the substrate speed for (A-F) are 1.2 kV, 80 μL/h, and 30 mm/s, respectively. The tip-to-collector distance and solution concentration for (A-C) and for (D-F) are 5 mm & 12 wt% and 3 mm & 8 wt%, respectively. Scale bar, 1 mm.

As a whole, the ability of direct-writing orderly lines or some other regular structures as required is preferred for a myriad applications, such as developing various layouts in microelectronic devices.

## IV. CONCLUSIONS

In summary, we have compared the modified NFES and the conventional NFES in direct-writing micro/nano structures from PVDF solution systems. The modified NFES is capable of writing various orderly micro/nano patterns, such as straight and continuous lines, parallel lines, beads-on-string structures, whereas the conventional NFES is difficult to give a continuous writing process. The great difference are closely related to the way in initiating the jet and solution supply, i. e. the jet initiated in the modified NFES process is first by mechanically drawing a jet and maintained by immediately applied electric field on continuously supplied droplets; however, the jet formed in the conventional NFES is started by the electric field applied and hindered by the limited solution on the spinneret. Through finely tuning the key parameters during the modified NFES process, such as the solution property, speed of the movable collector, and the distance between the spinneret and the collector, it is likely to construct complex patterns as required on various substrates, which overcomes the drawbacks of the conventional nanofabrication technique like electron-beam lithography (which is relatively slow, complicated and expensive).

## ACKNOWLEDGMENTS

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