

Micro/nanoscale continuous printing: direct-writing of wavy micro/nano structures via electrospinning

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Abstract. Micro/nanofibers that are created by direct-writing using an electrospinning (ES) technique have aroused much recent attention, owing to their intriguing physical properties and great potential as building blocks for micro/nanoscale devices. In this work, a wavy direct-writing (WDW) process was developed to directly write wavy micro/nano structures suitable for the fabrication of micro/nanoscale devices. The low voltage WDW technique is anticipated to be useful for a broad range of applications including flexible/stretchable electronics, micro optoelectronics, nano-antennas, microelectromechanical systems (MEMS), and biomedical engineering.

1. Introduction

The efficiency and low-cost production of micro/nanostructures by electrospinning (ES) via a direct-writing process has gained popularity recently, owing to its enormous potential for application in many fields. ES is considered to be a straightforward, low-cost technique to fabricate ultra-thin fibers with diameters ranging from tens of nanometers to several micrometers. In particular, having the ability to deposit functional materials directly and without contact on a variety of substrates, including flexible substrates, ES can be used to directly print large-area organic semiconducting nanowire arrays on device substrates, enabling sophisticated large-area nanowire lithography for nanoelectronics [1, 2]. Thus, ES is considered to be a promising alternative to traditional lithography technology to produce the microelectronic devices in an ingenious and cost-effective way. However, owing to the bending instability of a charged jet under coupled multi-field forces, the ES process is unstable and almost uncontrollable. Serpentine/wavy structures show enormous potential for applications in flexible/stretchable electronics owing to their excellent mechanical and electrical properties and performance [3-5]. In order to get fibers to assume a specific serpentine/wavy structure, several exploratory studies have been carried out, yielding remarkable results and very long wave-shaped fibers have been successfully made [6-11]. Although the above work shows promise in fabrication of novel structures, challenges remain in stably producing the micro/nano scale serpentine patterns which frequency, amplitude and wavelength can be control precisely. In previous research, we supplemented a high voltage AC applied to auxiliary electrodes (with an input voltage exceeding 1 kV) to produce

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wavy fibers [12]. However, the resulting fiber pattern was not smooth enough and the scale was not small enough to meet the requirements for manufacture of micro/nano devices. Furthermore, owing to the large whipping angle and amplitude, the pattern of fibers exhibited waveform distortion.

In this study, we applied lower voltages to the auxiliary electrodes; the AC voltage was set to below 300 V and the DC voltage set to less than 1.5 kV. This method differs from traditional ES in that the jetted liquid fiber is pulled by a combination of the DC and AC electrical field forces, while the low voltage AC-DC coupling electric field constrains the bending of the jet to make it controllable. This low voltage wavy direct-writing (WDW) process can be effectively controlled by adjusting the substrate speed, as well as the magnitude and frequency of the applied AC field. WDW permits direct-writing of small size complex serpentine patterns, because the formerly unstable jet can be precisely oriented and positioned. What's more, unlike conventional drop on-demand-type jet printing techniques [13], WDW can print the serpentine patterns in continuous jet mode. This method is anticipated to be useful for a broad range of applications including flexible/stretchable electronics, micro optoelectronics, nano-antennas, MEMS, and biomedical engineering.

2. Experimental

2.1. Preparation

Polyethylene oxide (PEO) with an average molecular weight of 2 000 000 (Aladdin, Shanghai, China) was chosen for the preparation of the solutions. PEO fibers were electrospun using 3%-8% (w/w) concentrations of PEO in deionized water with 4 hours stirring at 20°C. The ground collector was made of chromium-plated glass. All samples were stored at 20°C.

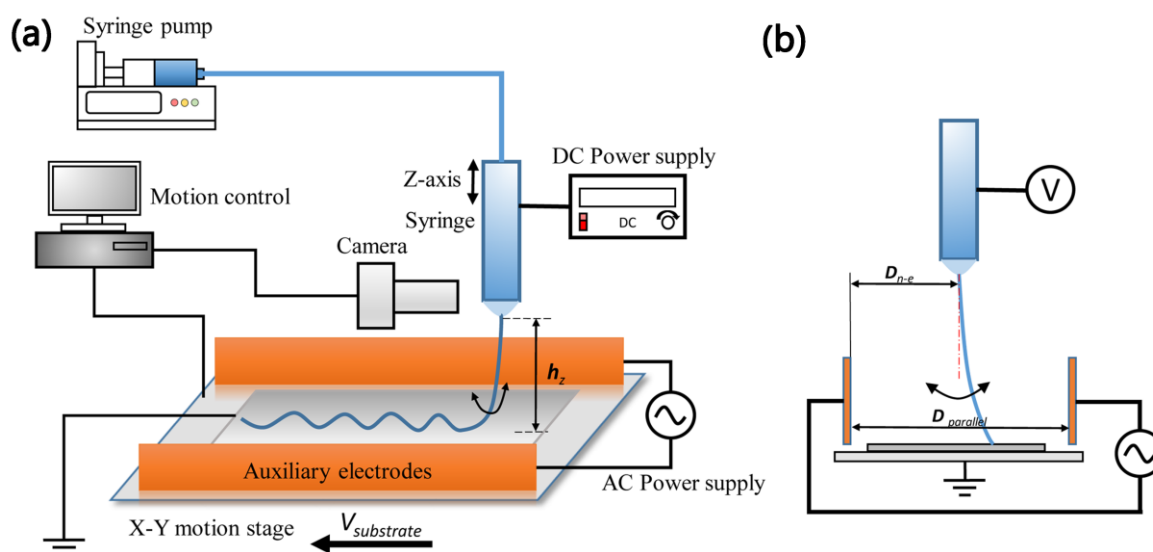


Figure 1. In this case simply justify the caption so that it is as the same width as the graphic.

2.2. Apparatus

The schematic diagram of the wavy direct-writing (WDW) apparatus is shown in figure 1. The PEO solution was delivered with a syringe pump (Lange, Inc., China). A stainless steel nozzle (inner diameter 260 μm and external diameter 520 μm) was adopted as an electrode, and the ground collector was a Cr-coated glass plate fixed to a moving stage (Suruga, Japan). A high voltage, generated by a direct current power supply (DW-P403, Dongwen Inc., China), was applied between the nozzle and the collector to generate a Taylor cone to assist in pulling out the jet from the nozzle. The nozzle-to-collector distance was adjusted to vary from 0-50 mm, and the moving speed of the substrate was adjusted from 0-400 mm s^{-1} . Furthermore, two parallel auxiliary electrodes made of copper foil were

stationed beside the collector and connected with an AC variable-frequency power supply (Sunan SNP-605, China).

2.3. Characterization

The microstructure was characterized by an image measurement instrument (Rational VMS-3020H, China) and scanning electron microscope (SEM) (Hitachi TM-3030).

3. Results and discussion

In this work, low voltage wavy direct-writing (WDW) is employed to achieve formation of the required serpentine patterns. Two parallel auxiliary electrodes made of copper foil are placed beside the collector and connected to an AC power supply, which can adjust the driving force acting on the fiber during the dropping process, as shown in figure 1b. The low voltage AC-DC coupling electric field constrains the bending of the jet, making it to become controllable. Therefore, WDW is able to directly write high-resolution serpentine patterns (figure 2). In the WDW process, the frequency of serpentine patterns is approximately equal to the frequency of AC electric field and the amplitude of the patterns depends linearly on the applied AC voltage value. The pattern wavelength can be controlled precisely by changing the speed of the collector.



Figure 2. Optical images of the morphology of the serpentine microstructure.

What's more, we found that the formation behaviour of the serpentine structures depended greatly on the strength of the AC electric field and the force status of the charged jet. With optimal DC voltage and nozzle height, the controllability of the whipping jet instability mainly correlates with the spacing of the two auxiliary electrodes, $D_{parallel}$, and D_{n-e} , the horizontal distance between the nozzle and auxiliary electrodes. When the two auxiliary electrodes are far apart or the D_{n-e} is large, the AC electric field has almost no effect on the charged jet, and repulsive electric forces between the uniformly-distributed charges play the leading role in influencing electrical bending, as shown in figure 3(a). This AC electric field effect becomes more and more apparent after a decrease in the distance between the nozzle and auxiliary electrodes, as shown in figures 3(b) and 3(c). When D_{n-e} falls below a specific distance, d , the AC electric field force is dominant and the path of the charged jet can be precisely controlled. The near-perfect serpentine pattern direct-write by WDW is shown in figure 2, but it was influenced by many possible factors and currently it is not possible to define the stability critical condition.

When $D_{parallel}$ and D_{n-e} are both optimal values, the nozzle-to-substrate distance, h_z , will greatly impact the movement of the charged jet. However, when h_z is lower than a specific height (in our experiment, 2 mm), WDW converts to NFES and the AC-DC coupling electric field barely influences the charged jet swing, as shown in figures 4(a) and 4(b). When h_z is huge, the system behaves as a conventional far-field ES with uncontrollable bending instability.

Additionally, solution concentration and collector speed also play important roles in the formation behaviour of the serpentine structures. When concentration is just lower than the critical value, bending superposition is observed in the direction of the jet path of motion, as shown in figures 4(e), 4(f) and 4(g). Under high substrate speed conditions, WDW converts to Mechano-Electrospinning (MES) [10, 14] and the AC-DC coupling electric field has almost no effect on controlling the charged jet swing. In particular, thinner and better-aligned nanofibers result from MES than NFES in an AC-DC coupling electric field, as shown in figures 4 (c) and 4(d).

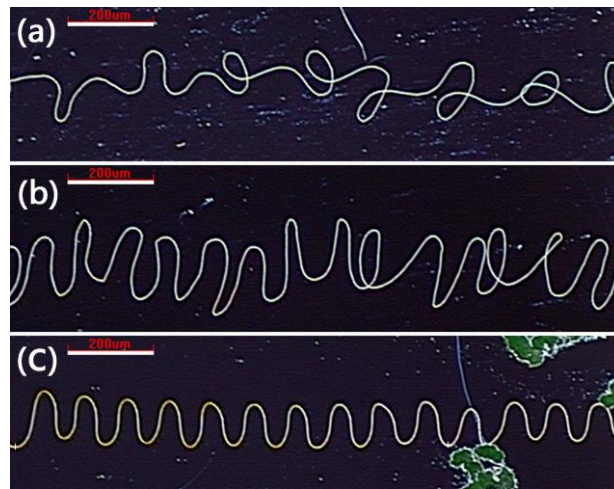


Figure 3. Optical images of the morphology of the microstructure with different distance between the nozzle and auxiliary electrodes: (a) 11 mm; (b) 9 mm; (c) 7.5 mm.

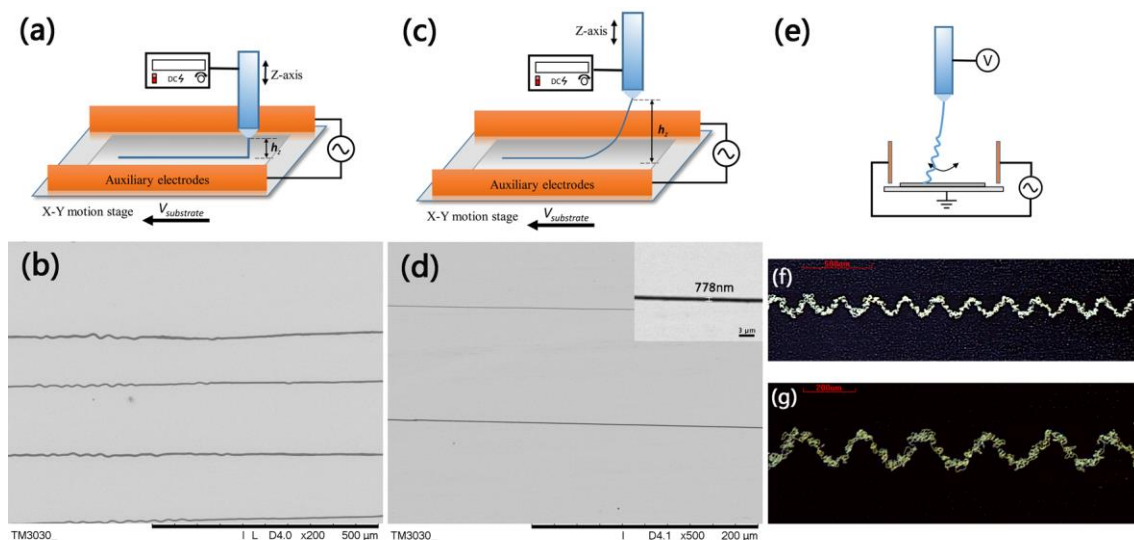


Figure 4. (a)(c)(e) Schematic diagrams of WDW in different condition. (a)(b) WDW converts to NFES when the h_z is lower than a specific height. The nanofibers arrays deposited in the condition: AC voltage 1 KV, DC voltage 1.5 KV, 4% PEO, nozzle-to-substrate distance 2 mm and substrate speed 10mm s^{-1} ; (c)(d) Under high substrate speed conditions, WDW converts to MES. The parallel nanofibers arrays deposited in the condition: AC voltage 1 KV, DC voltage 1.5 KV, 4% PEO, nozzle-to-substrate distance 5mm and substrate speed 30mm s^{-1} ; (e)-(g) when concentration is just lower than the critical value, bending superposition is observed and the patterns deposited are coarse. The fiber patterns deposited in the condition: 3% PEO, DC voltage 1.5 KV, AC voltage 300 V, 50 Hz, substrate speed 12mm s^{-1} and nozzle-to-substrate distance 5 mm.

4. Conclusion

In this study, we have developed the low voltage WDW process to directly write serpentine micro/nano structures suitable for the fabrication of micro/nanoscale devices and demonstrated the ability of low voltage WDW to precisely pattern nanofibers on substrates. This fabrication ability will permit the use of electrospun nanofibers based wiring of structural and functional components in microelectronics, MEMS, sensor, micro optoelectronics devices and biological apparatus.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (51305084), Project on the Integration of Industry, Education and Research of Dongguan City (No. 2013509109101), Guangdong Innovative Research Team Program (No. 201001G0104781202), Guangdong Provincial Key Laboratory of Micro-nano Manufacturing Technology and Equipment ((GDMNML2013-1, Guangdong Provincial Key Laboratory Construction Project of China (Grant No. 2011A060901026)), Key Joint Project of National Natural Science Foundation of China (Grant No. U1134004), China Post-Doctoral Science Foundation (125032).

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