One-Step Fabrication of Branched Poly(vinyl alcohol) Nanofibers by Magnetic Coaxial Electrospinning

Huijun Wu,[1,2] Jintu Fan,[2] Xianfu Wan,[2] Ning Du[3]

[1]College of Civil Engineering, Guangzhou University, Guangzhou 51006, China
[2]Institute of Textiles and Clothing, Faculty of Applied Science and Textiles,
The Hong Kong Polytechnic University, Hong Kong, China
[3]School of Mathematics and System Science, Shandong University, Jinan 250100, China

ABSTRACT: Branching has been emerging in 3-D interconnecting building blocks. Branched and hyperbranched poly(vinyl alcohol) (PVA) nanofibers were fabricated by coaxially electrospinning two-liquids under an alternating magnetic field in a facile manner. Both the PVA nanofiber trunks with diameter of 100–200 nm and the PVA nanofiber branches with diameter of 10–30 nm were formed in a single step. The length and the morphology of the branched PVA nanofibers could be controlled through a rational design of the magnetic field. The facile technique may readily be extended to prepare 3-D branched nanofibers from other materials such as various polymers and polymer–ceramic materials. Moreover, the multifunctional and multicomponent materials with branched nanostructure could be expected by using the magnetic coaxial electrospinning technique. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1425–1429, 2012

Key words: nanotechnology; nanofibers; branched; electrospinning; poly(vinyl alcohol)

INTRODUCTION

Branching is everywhere in nature. From riverbeds to oilfields, from trees and feathers to blood vessels, branching connects the large to the small.[1] Inspired by nature, the branched semiconductor nanocrystals or nanowires have recently been developed to increase structural complexity and enable much greater functionality.[2] The branched nanostructures were formed via multistep self-assembled growth process such as the vapor–liquid–solid (VLS) and solution–liquid–solid (SLS) methods.[3,4] The methods use initial seeding (e.g., catalytic nanoparticles) to form trunks followed by the sequential seeding to form branches. An electrospinning technique combined with subsequent catalytic process has recently been reported to fabricate the branched structure of carbon nanotubes on carbon nanofibers.[5,6] The majority of methods for the formation of branched nanostructure rely on the multiapplications of metal catalysts, which invariably lead to a multistep approach and much complexity owing to the rational design of either trunks or branches via specific chemical process. Moreover, these methods may work well in the fabrication of branched nanocrystals or nanowires for groups IV, III–V, and II–VI inorganic materials and carbon nanotube/nanofibers, but present difficulty in achieving branched nanofibers from polymers. Efficient and facile methods for the fabrication of branched nanofibers from polymers are essential for the development of various multifunctional materials and integrative devices.

Although electrospinning[7,8] has been extensively applied to manufacture various nanomaterials including nanofibers, hollow tubes, core-shell structured nanofibers, and multi-channel tubular nanofibers,[9–15] little work has been directed toward the fabrication of branched nanofibers. The majority of relevant publications concentrate on the irregular splitting and branching at scales from millimeters to micrometers.[16,17]

In this work, we demonstrate for the first time the capabilities of the so-called magnetic coaxial electrospinning technique comprising electrohydrodynamically generated coaxial two-liquid jets and magnetic field induced branches to produce polymeric nanofibers with branched nanostructure. The novelty lies in that the compound two-liquid jets made of magnetized polymer solution on the outside and polymer solution in the inside is electrospun in an alternating magnetic field, which yields both the trunks and the branches in one step without the need of molecular-level assembly.
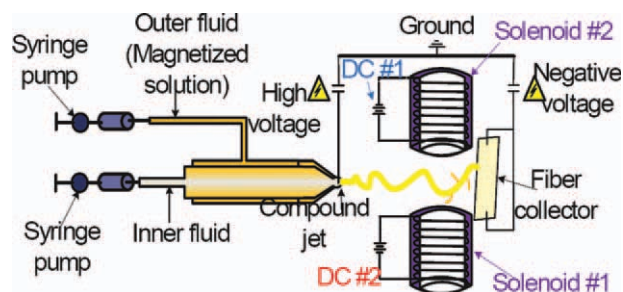
Figure 1 Schematic illustration of electrospinning technique for forming branched nanofibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

The aqueous poly(vinyl alcohol) (PVA) solution was used as the inner liquid for coaxial electrospinning, while the magnetized PVA solution prepared by adding a small mount of magnetite nanoparticles was used as the outer liquid. The PVA ($M_w \approx$ 90,200, 98–99% hydrolyzed) was manufactured by Sigma-Aldrich Company (St. Louis, MO). The Fe_3O_4 nanoparticles (average diameter $\approx$ 20 nm) were manufactured by Kaier Nanometer Energy and Technology Company (Hefei province, China).

The inner liquid was prepared by dissolving 1.6 g PVA powder in 18.4 g distilled water in a capped bottle. The solution was magnetically stirred at 80°C for 6 h and then cooled to room temperature. The outer liquid was prepared by dispersing 40 mg Fe_3O_4 nanoparticles to the as-prepared aqueous PVA solution under the ultrasonical stirring for 6 h.

The experimental setup for fabricating branched PVA nanofibers is sketched in Figure 1. The coaxial capillary tips were used to feed the two liquids independently through two syringe pumps. The as-prepared inner and outer liquids were pumped out at the flow rates of 0.9 and 0.1 mL h^{-1}, respectively. The outer nozzle was connected to the cathode of a positive high voltage generator (EMCO High Voltage Corporation, Canada), and a metallic plate covered with aluminum foil as the fiber collector was connected to a negative high voltage generator (EMCO High Voltage Corporation, Canada). The counter-electrodes of both the positive and negative voltage generators were grounded. The positive and negative voltages were set at 15–20 kV and −2 to −5 kV, respectively. The working distance between the nozzle tip and the collector was 15–18 cm. Two solenoids (crane model magnet, manufactured by Zonhen Electric Appliance, Shenzhen, China) with spacing of 3–4 cm were placed symmetrically at both sides of the collector. The two solenoids were independently powered by two 12 V direct current power supplies. The magnitude of the magnetic field

at the middle of the two solenoids varies in the range about 0.8–2.0 T with a typical value of 1.4 T.

The key of the fabrication technique was the control scheme of the alternating magnetic filed to stretch the magnetized polymer solution on the outside. The control scheme of the power supply for the two solenoids is demonstrated in Figure 2. In a typical technique, the solenoid #1 first worked for the preset working period (t_1) and then was closed. After the solenoid was closed for a preset interval period of (t_{10}), the solenoid #2 began to work. Similarly, the working period and the interval period of the solenoid #2 were preset t_2 and t_{20}, respectively. The alternating magnetic was generated by controlling the working and interval periods of the two solenoids. The controllable alternating magnetic field was applied for the first time for electrospinning branched nanofibers in this work.

The morphology of the nanostructure of the electrospun nanofibers was investigated by using a field emission scanning electron microscopy (SEM, JEOL JEM-6335F) at an accelerating voltage of 3–5 kV after coating the nanofibers with gold. Transmission electron microscopy (TEM; JEOL JEM-2010 microscopy) operated at a 120-kV accelerating voltage was also used to characterize the nanostructure of the branched nanofibers.

RESULTS AND DISCUSSION

Figure 3 shows a typical field emission scanning electron microscope image of the branced nanofibers fabricated by one-step magnetic coaxial electrospinning as the working and interval periods of the magnetic field (#1 and #2) are both preset at 0.4 s. It can be found that several tiny branches of the PVA nanofibers were branched out of the PVA nanofibers. Compared to the previous arts about branched nanofibers fabricated by multistep VLS, SLS methods, and electrospinning followed by catalytic processes, this magnetic coaxial electrospinning
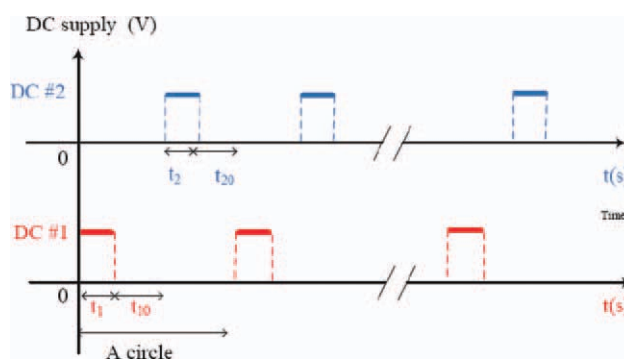

Figure 2 Control scheme of magnetic filed for electrospinning branched nanofibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
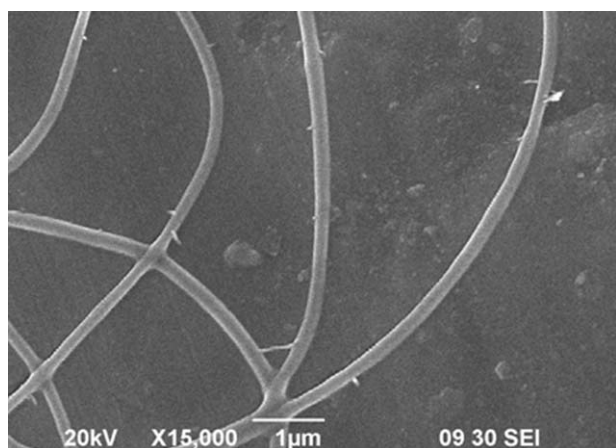
Figure 3 SEM image of branched nanofibers fabricated by one-step magnetic coaxial electrospinning.

technique enabled the formation of 3-D branched fibers at the nanometer scale in a single step.

The TEM images of the PVA nanofibers with the branched nanostructure fabricated by the one-step magnetic electrospinning are shown in Figures 4
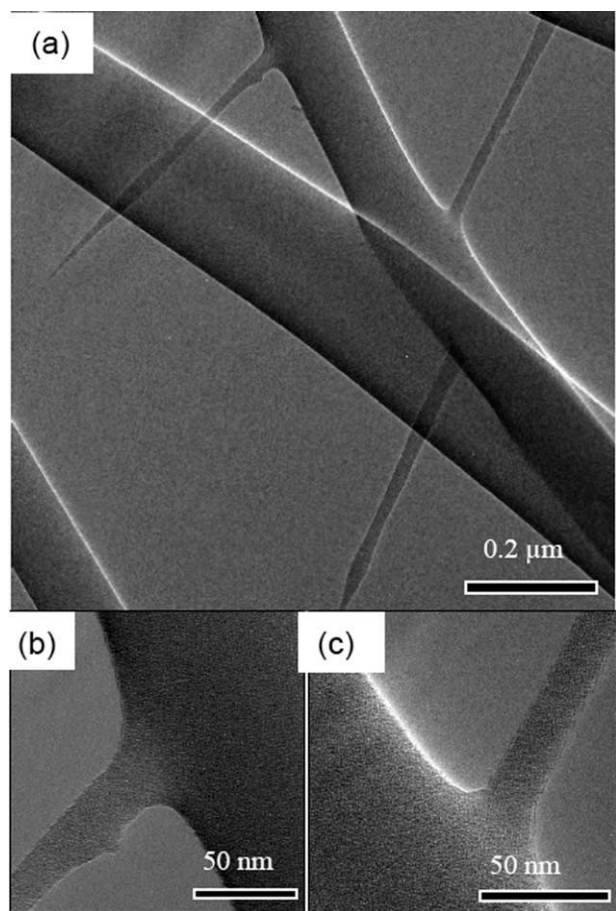

Figure 4 TEM images of branched nanofibers fabricated under the magneti c field scheme as the working and interval periods are both 0.4 s. (b,c) are magnified view of junctions in (a).
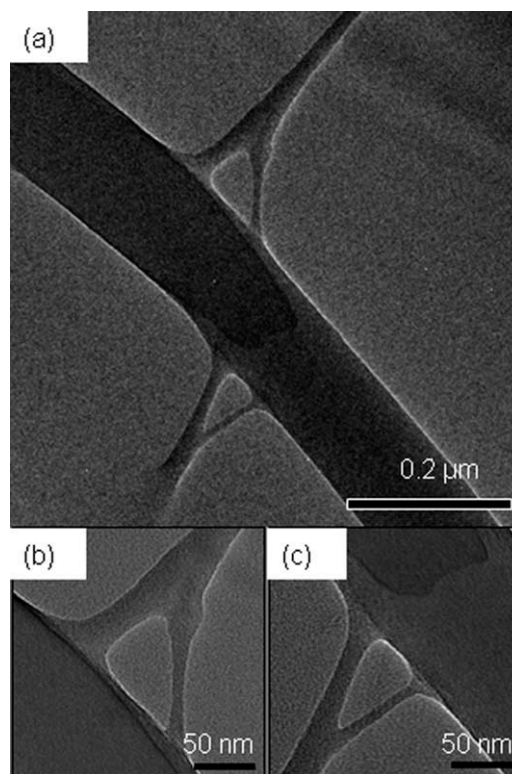

Figure 5 TEM images of branched nanofibers fabricated under the magnetic field scheme as the working and interval periods are both 0.05 s. (b,c) are magnified view of junctions in (a).

and 5. Figure 4 shows a typical TEM image of the branched PVA nanofibers as the working and interval periods of the magnetic field (#1 and #2) are both preset at 0.4 s. The branches can be observed at both sides of the trunk of the PVA nanofibers. The diameters of the trunks and branches were 100–200 nm and 10–30 nm, respectively.

The alternating magnetic field played an important role on the formation of the branches from the magnetized liquid. As the working and interval periods of the magnetic field (#1 and #2) were shortened to be 0.05 s, the branched nanofibers with two-point junctions among branches and trunks could be formed. Figure 5 shows a TEM image of a typical structure of the two-point jointed branches. During the magnetic coaxial electrospinning process, the formation of the branched structure was dependent on the simultaneous processes of the evaporation of solvent, elongation of solidifying fibers,[7,17] and the splitting and breaking of branches from the surface of the compound jets. When the magnetic field alternated fast enough, the interval period may not be sufficient for the magnetized branches to split and solidify completely. As a result, the two-point jointed branches could be formed.

If a hybrid control scheme of the working and interval periods of the magnetic field were
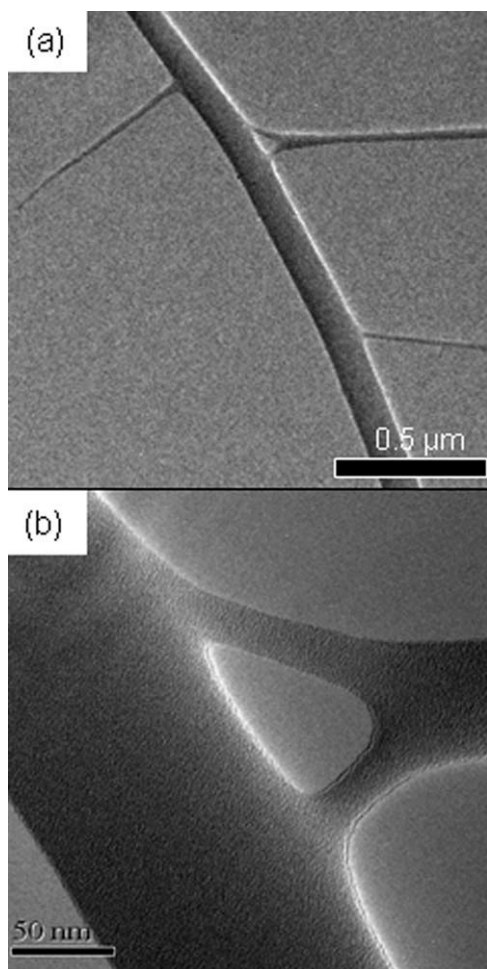
Figure 6 TEM images of typical branched nanofibers with hybrid one-point and two-point junctions; (b) is magnified view of the two-point junction in (a).

Figure 7 TEM images of hyperbranched nanofibers formed under different magnetic field scheme as the working and interval periods are 1s and 0.4 s, respectively; (b) is magnified view of hyperbranches in (a).

the junction between the primary branch and the trunk.

It should be noted that in the one-step magnetic electrospinning method of fabricate branched nanofibers, rational design of the flow rates of both inner and outer fluids is critical to the successful fabrication of branched nanofibers. To ensure the outer fluid to be split and cut perfectly from compound jets to form regular branches, the flow rate of the outer fluid (0.1 mL/h) should be much lower than that of the inner fluid (0.9 mL/h). Consider the small quantity of magnetic nanoparticles used in the outer fluid (i.e., 0.4 wt %[18]), we do not anticipate that the presence of magnetic nanoparticles has significant adverse impact on the properties of the as-formed nanofibers for most applications.

conducted, a hybrid-branched nanostructure with hybrid one-point and two-point junctions could be obtained. The hybrid PVA-branched nanostructure with hybrid one-point and two-point junctions is shown in Figure 6, which occurred under the magnetic filed control scheme as $t_1 = 0.1$ s, $t_{10} = 0.4$ s, $t_2 = 0.2$ s, and $t_{20} = 0.3$ s.

The length of the branches could also be adjusted by varying the working periods of the alternating magnetic filed. Figure 7 shows a TEM image of the branched nanofibers when the interval period of the magnetic field was kept the same as that in Figure 4, yet its working period was prolonged to 1 s. The lengths of the branches in Figure 7 varied in the range of 1.0–1.5 μm, which was about twice as long as those in Figure 4. Moreover, because the electric and magnetic fields stretch the compound liquid jets at high stretching rates during the magnetic coaxial electrospinning process, hyperbranching may occur. Figures 7 and 8 show the tiny hyperbranches with lengths of about 15 nm on the primary branch and
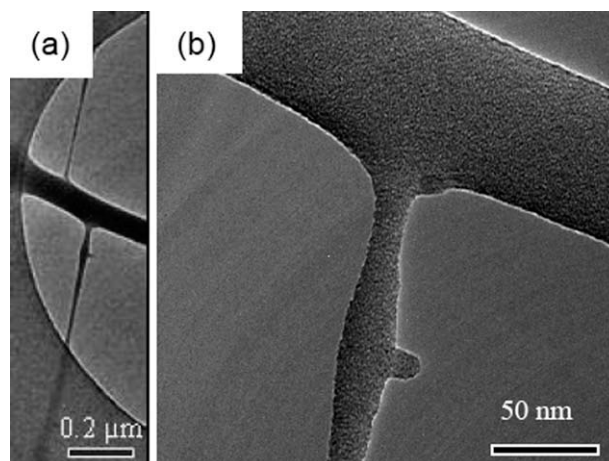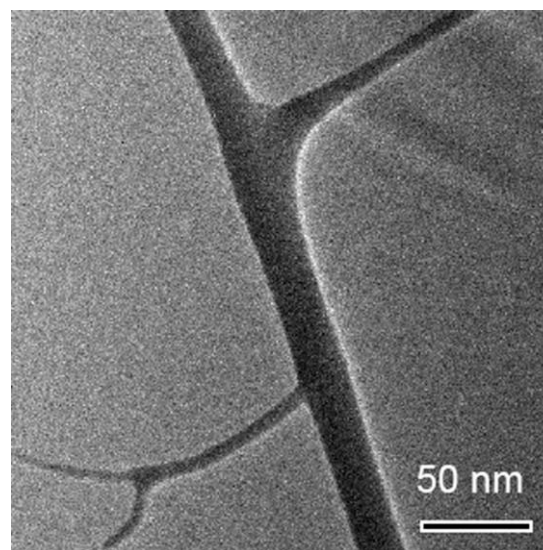

Figure 8 TEM images of hyperbranched nanofibers formed under different magnetic field scheme as the working and interval periods are 0.25 and 0.4 s, respectively.

CONCLUSIONS

A facile and single-step magnetic coaxial electrospinning technique was demonstrated for fabricating the branched and hyperbranched nanofibers from PVA. Both the nanofibers trunks with diameter of 100–200 nm and the nanofibers branches with diameter of 10–30 nm were formed from the PVA in a single step. The technique allows the control of the branch lengths and the junction morphology through a rational design of the magnetic field. It could be readily extended to other polymers and polymer–ceramic composites to form 3-D branched nanofibers in various applications such as materials to mimic the branching of feathers and down for super-light insulations, biomedical materials for multicomponent drug delivery and tissue engineering, high efficient catalysts, and advanced electric and photonic devices.

References

1. Warburton, D. Nature 2008, 453, 733.
2. Wang, D.; Lieber, C. M. Nat Mater 2003, 2, 355.
3. Wang, D.; Qian, F.; Yang, C.; Zhong, Z. Nano Lett 2004, 4, 871.
4. Wei, D. C.; Cao, L. C.; Fu, L.; Li, X. L.; Wang, Y. Adv Mater 2007, 19, 386.
5. Hou, H. Q.; Reneker, D. H. Adv Mater 2004, 16, 69.
6. Ostermann, R.; Li, D.; Yin, Y. D.; McCann, J. T. Nano Lett 2006, 6, 1297.
7. Reneker, D. H.; Yarin, A. L. Polymer 2008, 49, 2387.
8. Greiner, A.; Wendorff, J. H. Angew Chem Int Edit 2007, 46, 5670.
9. Wu, H. J.; Fan, J. T.; Du, N. J Appl Polym Sci 2007, 106, 576.
10. Wu, H. J.; Fan, J. T.; Qin, X. H.; Zhang, G. G. Mater Lett 2008, 62, 828.
11. Wu, H. J.; Fan, J. T.; Qin, X. H.; Mo, S.; Hinestroza, J. P. J Appl Polym Sci 2008, 110, 2525.
12. Jayaraman, K.; Kotaki, M.; Zhang, Y. Z.; Mo, X. M.; Ramakrishna, S. J Nanosci Nanotechnol 2004, 4, 52.
13. Teo, W. E.; Ramakrishna, S. Nanotechnology 2006, 17, R89.
14. Wu, H. J.; Fan, J. T.; Chu, C. C.; Wu, J. J Mater Sci Mater M 2010, 21, 3207.
15. Li, D.; Xia, Y. Adv Mater 2004, 16, 1151.
16. Koombhongse, S.; Liu, W. X.; Reneker, D. H. J Polym Sci, Part B Polym Phys 2001, 39, 2598.
17. Yarin, A. L.; Kataphinan, W.; Reneker, D. H. J Appl Phys 2005, 98, 064501.
18. Yang, D. Y.; Lu, B.; Zhao, Y.; Jiang, X. Y. Adv Mater 2007, 19, 3702.