Strategy for the development of stretchable highly aligned electrospun polyacrylamide (PAM) nanofibers

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This paper reports the alignment of PAM micro/nanofibers using electrospinning techniques. Gaining alignment of micro/nanofibers is a critical step for their utilization in different applications. We report electrospinning approach with modified collector structure to get PAM fibers aligned. A collector with two conductive strips separated by small void channels on rotating disk has been used to create symmetrical distribution of electric field on both sides of the conductive strips which resulted in highly aligned fibers formation. We believe, this method provides a good control on the alignment of micro/nanofiber formation.

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1. Introduction

Recently due to new advancement in nanotechnology, researchers are interested in fabrication of polymer fibers in nano scale which has versatile applications in sensing, photonic, bio-engineering and separation [1-4] etc. Different processing techniques are used to make polymer nanofibers for example, self-assembly [5,6], phase separation [7,8], drawing [9,10], and template synthesis [11,12]. The main disadvantage of these techniques is that scaling up process has not been developed up to now and there is no proper control of fiber dimension during fiber formation. To overcome these problems, electrospinning technique is preferred which uses electrostatic forces to spin polymer micro/nanofibers. Polymer micro/nanofibers fabricated from electrospinning method have been applied in fascinating ways, such as for fuel cells [13], bio-engineering compositions [14,15], energy harvesting [16], sensing [17], textiles [18,19], lasing [20], filtration [21,22], immobilization of enzymes [23], electrolytes [24] and tissue regeneration [25]. In a conventional electrospinning method, the polymer solution is filled in a syringe and the syringe is placed in a syringe pump which is used to control the flow rate of solution. The solution is forced towards needle of small diameter to form a drop at the needle tip. A high voltage is connected to needle and ground is connected to collector. When high voltage is applied, the polymer solution becomes charged. With the increase of applied voltage, the electric field reaches at required critical value to overcome the surface tension of polymer solution and a jet of polymer solution emerges out from the tip. The ejected solution undergoes stretching and elongation action which enables the jet to form a long nano scale fiber that is attracted towards collector. Solution, process and ambient parameters during electrospinning play an important role in achieving smooth and ultrafine micro/nanofibers [26,27].

It is simple, cost effective and large scale production technique. By using this method, micro/nanofibers of different morphology and structures like hollow micro/nanofibers [28], core shell nano fibers [29,30] and beaded nanofibers have been fabricated and their diameter can be easily tuned by controlling different parameters [31]. Despite the fact that electrospinning is viewed as a powerful and mass production technique for the fabrication of polymer micro/nanofibers, fibers alignment issue still should be overcome for applications. Electrospun micro/nanofibers are usually random without structural alignment which is adverse because highly aligned and well oriented micro/nanofibers can prompt higher molecular order and crystallinity [32] for better mechanical, electrical and optical properties as compared to randomly deposited micro/nanofibers. Current research shows that electrospun micro/nanofibers can be aligned by designing a special collector structure.

Recently several alignment methods for electrospinning have been directed for different polymers but for the alignment of polyacrylamide (PAM) micro/nanofiber, no proper method has been described yet according to our knowledge. PAM is known as a good host for nanophotonics, so there is a need of highly aligned PAM micro/nanofibers to achieve the best performance. Keeping this in mind, a method is reported to obtain highly aligned PAM electrospun micro/nanofibers. Nanosensors provide better sensitivity with aligned micro/nanofibers [33]. P. Katta et al. have demonstrated a collector in cylindrical shape with copper wires which are evenly spaced [34] but alignment of fibers is lost for thicker mats. Polyetherimide electrospun fibers have been aligned by using rotating grounded collector [35]. B. Sundaray et al. have reported that cylinder wrapped with plastic film is connected to the axle of DC motor as a substrate. This substrate is rotated with high speed and aligned micro/nanofibers are obtained [36]. Rotating cylinder enables the deposition of micro/nanofibers over large surface area comparatively but getting well aligned fibers on that cylinders seems to be challenged because the pitch among micro/nanofibers is varied during this method. Steel blades can be used to control electric field in order to obtain aligned fibers [37]. D. Yang, et al have reported the magnetic electrospinning concept with magnetic-particles doped polymer solution by using two grounded magnets as a collector. The magnetized micro fibers are stretched to align microfibers across the magnet bars [38]. D. Edmondson et al. have reported a concept of centrifugal electrospinning to fabricate well-aligned polymer micro/nanofibers over large area [39]. Aligned polyacrylonitrile (PAN) electrospun fibers have been studied with using two conductive plates isolated by gap [40].

Our main goal is to obtain aligned PAM electrospun micro/nanofibers. In this paper we have reported a method for the formation of aligned PAM micro/nanofiber by using two conductive stripes as a collector on rotating disk. The effect of controlling parameters on fiber diameter was observed. We also investigated the stretching ability of PAM electrospun micro/nanofibers by stretching the PDMS substrate.

2. Experimental

Polyacrylamide (Pcode 92560, C.No. 9003-05-8, Sigma- Aldrich**)** was used to make micro/nanofibers. Distilled water was used as a solvent. Polymer solution was mixed by adding PAM and distilled water. After stirring for 5 hours polymer solution was ready for electrospinning. KD Scientific syringe pump was used to control feed rate. High voltage DC power supply was used to provide electric potential and Nikon optical microscope was used to see micro/nanofibers. The experimental apparatus for electrospinning procedure is shown in fig. 1(b). Polymer solution was filled in 2.5 mL plastic syringe and carried by syringe pump which forced the solution to eject out. Positive terminal of power supply was connected to the needle of syringe and negative terminal was connected to the rotating disk collector.

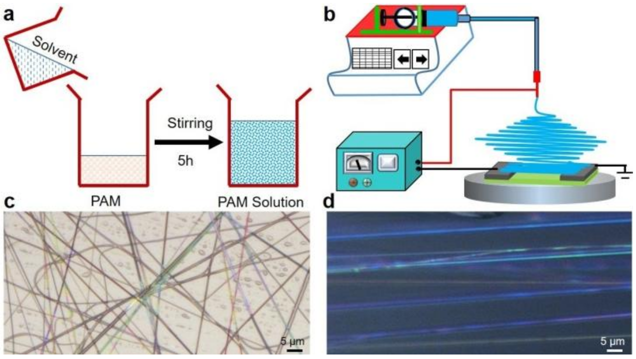

Fig. 1. Schematic demonstration of aligned PAM electrospun fiber formation. (a) Polymer solution preparation. (b) Experimental apparatus for electrospinning procedure. (c) Microscopic image of random micro/nanofibers directly on substrate. (d) Microscopic image of suspended aligned micro/nanofibers (color online)

When voltage was applied to the apparatus, polymer solution was charged and made a drop at the tip of needle. As voltage was increased, electrostatic forces were reached at a critical point to overcome the surface tension of polymer solution and solution was ejected out from the needle tip. After that solution was encountered with stretching and elongation process. In this way long and random micro/nanofibers were deposited on the collecting substrate. To obtain aligned micro/nanofibers, the structure of collector was changed. An insulated substrate with small channels was prepared with stripes to suspend micro/nanofibers in air. These stripes were wrapped with aluminum tape to make conductive and connected to the ground. This collector substrate was placed on the insulated rotating disk and well aligned micro/nanofibers were obtained between the conductive stripes.

3. Results and discussions

In the typical electrospinning procedure, jet of polymer was emerged out from the needle tip with the increase of electric forces. Due to instability, jet moves straightforward prior to bend and whip which resulted in the random deposition of micro/nanofibers on collector. In this typical process, electric potential between the tip of needle and collector is same for whole area on circle from the central point of the needle tip. Electric field has no special orientation towards collector, as a result, random fibers are deposited. So, it is hard to control the polymer jet direction and especially making it straight towards collector. Nevertheless, by changing collector with parallel conductive stripes, fibers are suspended across the channels and are well aligned. It is observed that deposited micro/nanofibers on parallel conductive stripes are more aligned than the other substrate because distribution of electric field is symmetrical on both sides of parallel conductive stripes [41,42]. When the charged fibers move towards electrodes, the opposite charges on the electrodes pull the micro/nanofibers across the gap of two electrodes [43]. The action of pulling forces as demonstrated by Jae-Hun Kim [44], during alignment of micro/nanofibers is modified with rotating disk and described in Fig. 2(a).

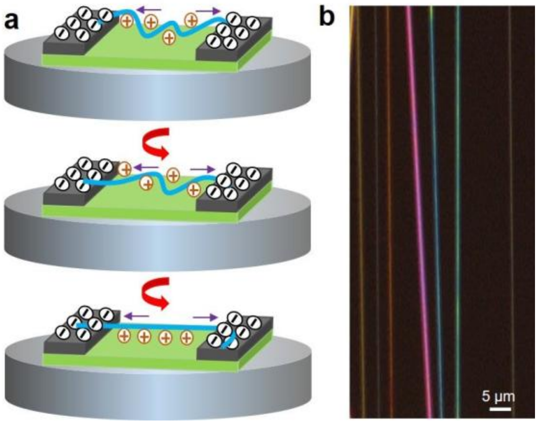

Fig. 2. Fiber alignment process. (a) Effect of electric field during alignment. (b) Microscopic image of aligned suspended polymer micro/nanofibers (color online)

It is investigated that alignment of micro/nanofibers is also affected by speed of rotating disk. At lower speed micro/nanofibers collapse with each other but with the increase of speed, alignment is increased because mechanical pull by disk exerts a pressure on the micro/nanofibers resulting in stretching, straightening and thinning of the micro/nanofibers. The morphology of micro/nanofibers is affected by solution viscosity. Beaded fibers are formed with lower viscous solution [45]. Polymer solution of four different concentrations as in Table 1 was prepared to check the effect of concentration on the fiber diameter.

Table 1. Effects of solution concentration on fiber diameter

Concentration (%)	Diameter (nm)
2	50
5	200
9	350
12	430

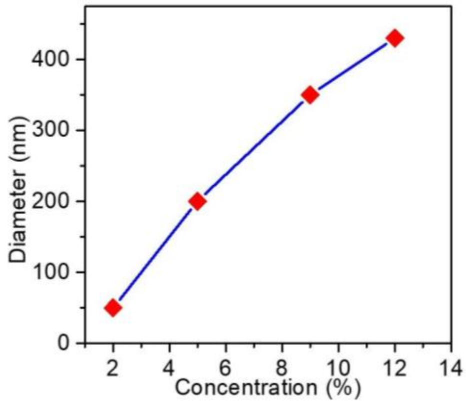

Fig. 3. Graph showing the linear relationship between fiber diameter and polymer solution concentration (color online)

It is observed that with lower concentration almost 1% beaded fibers are formed but with the increase of solution concentration, fine and smooth fibers are formed and diameter of fibers is also increased and shows a linear behaviour between diameter and concentration in Fig. 3.

The diameter of fiber is also affected with flow rate of solution and distance from tip to collector. Thin fibers are formed with lower flow rate and much time is available to evaporate the solvent [46]. Fiber diameter is increased with the increase of flow rate because more volume of polymer solution is ejected from the tip.

Table 2. Effects of distance from collector to needle tip on fiber diameter

Distance (cm)	Diameter (nm)
6	500
8	400
9	350
10	217

It is also observed that with the increase of distance from needle tip to collector, diameter of micro/nanofiber is decreased as shown in Fig. 4 because electrostatic forces are constant and have more space to evaporate solvent which results in increased bending instability of jet.

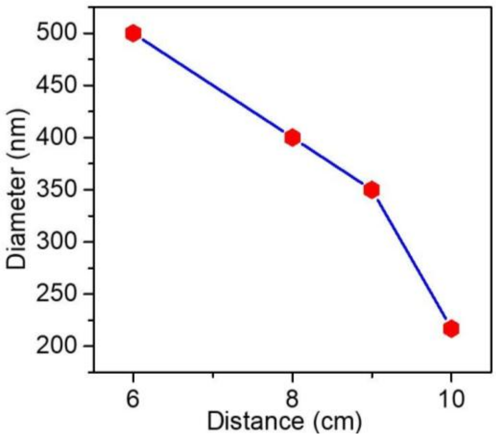

Fig. 4. Graph showing the relationship between fiber diameter and distance from collector to needle tip (color online)

Due to this micro/nanofibers undergo stretching and thinning and diameter of fibers is reduced. To check stretchability of PAM electrospun micro/nanofibers, we used the PDMS substrate as a collector with small channels so that micro/nanofibers could suspend across them. PDMS has property of flexibility. Micro/nanofibers were deposited on PDMS substrate during electrospinning process. When this substrate was stretched by applying force with 1Dimensional stage, the PAM fiber was also stretched and did not break. Micro/nanofiber diameter is decreased with the increase of stretching. This stretching ability will make the PAM micro/nanofibers to be used as a strain sensor.

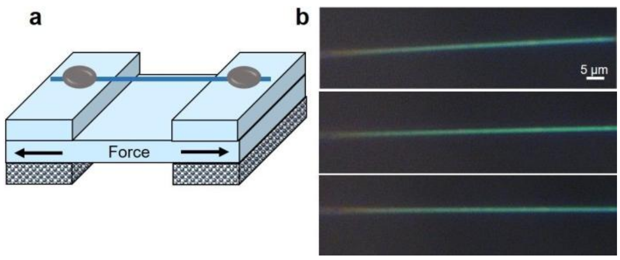

Fig. 5. (a) Schematic setup for mechanical stretching. (b) Microscopic images of PAM fiber during stretching at 0μm, 1.5μm and 3μm distance respectively

4. Summary

In summary, we devised a methodology for PAM micro/nanofibers alignment by modifying the structure of collector in electrospinning setup. It is simple, cost effective and scaling up process for fabricating smooth and aligned micro/nanofibers. Two conductive stripes separated by void channels were used to align microfibers. This method created the symmetrical distribution of electric field on both sides of the conductive stripes which resulted in highly aligned microfibers. The effects of governing parameters were also observed to get smooth and fine micro/nanofibers. At last the stretchability of PAM electrospun micro/nanofibers was checked by stretching the microfiber. Stretchable property of PAM electrospun micro/nanofibers will make them possible to use in strain sensing. This reported alignment method is expected to be a promising technique in future development of nano fiber based systems for communication and nanophotonics.

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