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AFM-based voltage assisted nanoelectrospinning

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Abstract

This paper describes an atomic force microscope (AFM) based voltage-assisted electrospinning technique. Single nanofibers on substrates are prepared via simultaneous preparation and deposition. In this work, an AFM-based electrospinning process is developed to generate polyethylene oxide (PEO) polymeric single fibers with nanometer scale diameters. The results demonstrate the feasibility of this developed approach for assembling nanofibers at predetermined positions. This work represents a promising advancement in nanomanufacturing of one-dimensional nanostructured materials for micro- and nanoscale devices.

Keywords: Atomic force microscopy; Fiber technology; Polymers; Nanomaterials

1. Introduction

Since the discovery of carbon nanotubes, there has been great interest in the synthesis of one-dimensional materials including nanowires, nanofibers, nanorods and nanobelts [1–3]. These one-dimensional nanoscale materials have fascinating properties and unique applications. Nanofibers and nanowires have emerged as important building blocks at the nanoscale, serving as interconnects and active components in nano-scale electronic, magnetic, and biomedical devices [4–6]. Recently, electrospinning of polymer fibers has been exploited as a unique and versatile approach for fabricating fibers with diameters typically ranging from nanometers to micrometers [7–9].

Precise control of the electrospinning process and *in-situ* manipulation and characterization of spun nanofibers continues to be a challenge. This is especially true concerning patterning over predetermined areas; nanofibers prepared via electrospinning for use in nano-scale devices continues to be problematic. This limits the potential applications of electrospinning as a manufacturing process for micro- and nanoelectromechanical systems [10–12]. An AFM can be used to deposit nanoparticles and molecules on a surface to form pattered nanostructures [13, 14]. Similarly, AFM assisted nano-electrospinning (ANES) has been developed to fabricate nanofibers in a controllable fashion via material deposition from an AFM probe.

2. Experimental details

Polyethylene oxide (PEO, M_w = 4,000,000) from Aldrich is used to prepare the polymer solutions. PEO was dissolved in deionized water to make a solution concentration of 0.08 wt.%. The solution was stirred for 5 h before electrospinning. Si (110) (5–10 Ω-cm) was used as a substrate for depositing the nanofibers. Nanoelectrospinning was performed by applying a bias voltage of 8 V, 10 V, and 12 V between the AFM tip coated with PEO solutions and the silicon substrate. Experiments were performed on an AFM system as described previously [15]. The spinning distance between the tip and the substrate was set at 10 μm, 15 μm, and 20 μm. The translational speed of the silicon substrate was 5 μm/s as prescribed by the servo controlled piezoelectric position stages. The nanoelectrospinning was performed under ambient conditions at 25°C and 40% RH. The morphology and microstructure of PEO nanofibers and deposits

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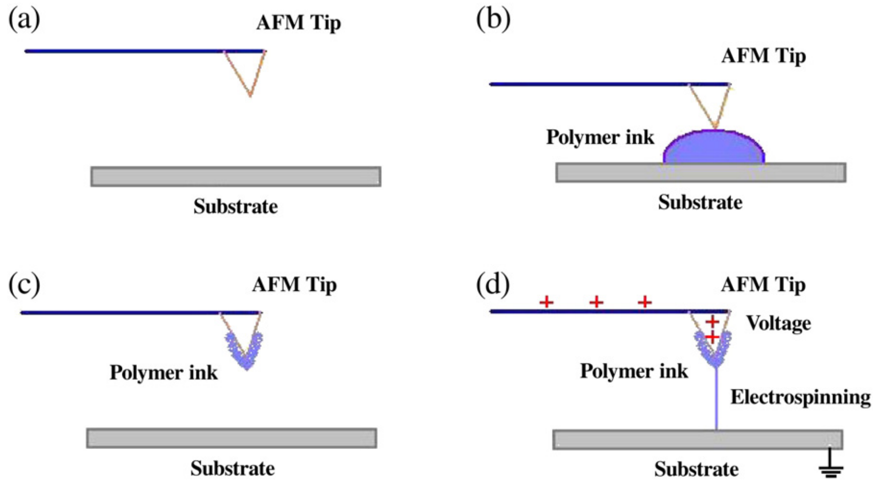

Fig. 1. Schematic illustration of atomic force microscope assisted nanoelectrospinning (ANES).

were characterized using scanning electron microscopy (SEM, FEI XL30 SEM-FEG) after gold coating.

3. Results and discussion

Fig. 1 shows a schematic illustration of the ANES process. A solution precursor is coated on the AFM tip in the custom AFM instrument. Then, a low voltage bias is applied between the tip and substrate to initiate the nanoelectrospinning of fibers in the cone-jet mode. This technique permits the on-demand fabrication and deposition of nanofibers under atmospheric conditions at specific locations on the substrate. The ability to spatially control the preparation and manipulation of nano-scale fibers is of great interest not only for electrospinning technology but also for the nanomanufacture and study of nanofiber characteristics.

The morphologies of the final products achieved through nanoelectrospinning vary significantly under different processing conditions. The microstructure of fibers prepared using a spinning voltage of 8 V and a spinning distance of 10 μm is shown in Fig. 2(a). The SEM image reveals that a straight PEO fiber with an average diameter size of 150±30 nm can be generated on the silicon substrate. The strength of the electrical field is 0.8 V/ μm, which is large enough to produce fibers via ANES. When the spinning distance was increased to 15 μm, a PEO polymer relic instead of electrospun fiber was produced, as shown in Fig. 2(b), demonstrating that ANES was not properly initiated, but micron-drip spraying was generated by the electrohydrodynamic atomization. As the spinning distance was increased to 15 μm, the strength of the electrical field became 0.53 V/ μm and was not strong enough to break up the PEO solution droplet. Therefore, the solution accumulated at the end of the AFM tip and lead to the formation of a droplet relic on the substrate [16]. While the spinning distance was further increased to 20 μm, nothing can be deposited on the silicon substrate due to the low electric field strength.

At a spinning voltage of 10 V, when the spinning distance was increased from 10 μm to 20 μm, the microstructure of the electrospun fibers changes from straight to beaded, as shown in Fig. 3, due to strength variations of the electrical field. Fig. 3(a) shows a SEM image of fiber produced using a spinning distance of 10 μm and a spinning voltage of 10 V. The fiber was generated and assembled in a line, with an average diameter of 430±15 nm. Fig. 3(b) shows a SEM image of PEO nanofiber prepared using ANES at a spinning distance of 15 μm (electrical field strength of 0.67 V/ μm). The image shows that nanofiber has a uniform diameter with an average diameter of approximately 200±10 nm, a reasonable dimension to be used in the fabrication of micron-scale devices [17]. When the spinning distance was 20 μm (electric field strength is 0.5 V/μm), a beaded fiber was generated on the substrate as shown in Fig. 3(c). The average fiber diameter and bead size was 250±20 nm and 2.3±0.3 μm, respectively. The beaded fiber structure is believed to be due to stretching and acceleration of a charged jet under a low electrostatic field before deposition, as the strength of the field was not sufficient to stretch the polymer into a straight fiber [18]. When the spinning voltage was increased to 12 V with a spinning distance of

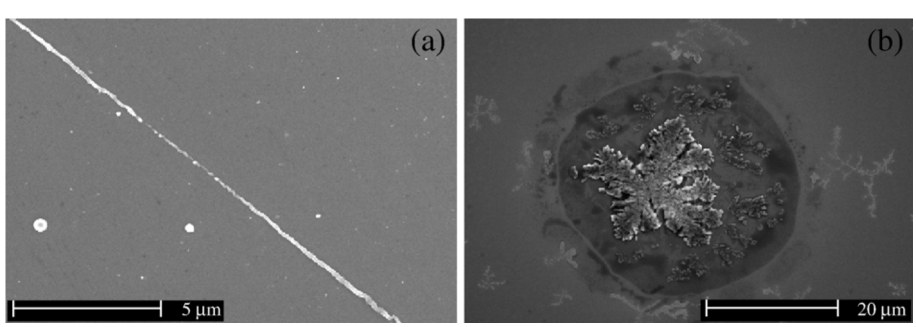

Fig. 2. SEM images of fiber and relic prepared via ANES using different parameters: (a) a spinning voltage of 8 V and a spinning distance of 10 μm; (b) a spinning voltage of 8 V and a spinning distance of 15 μm.

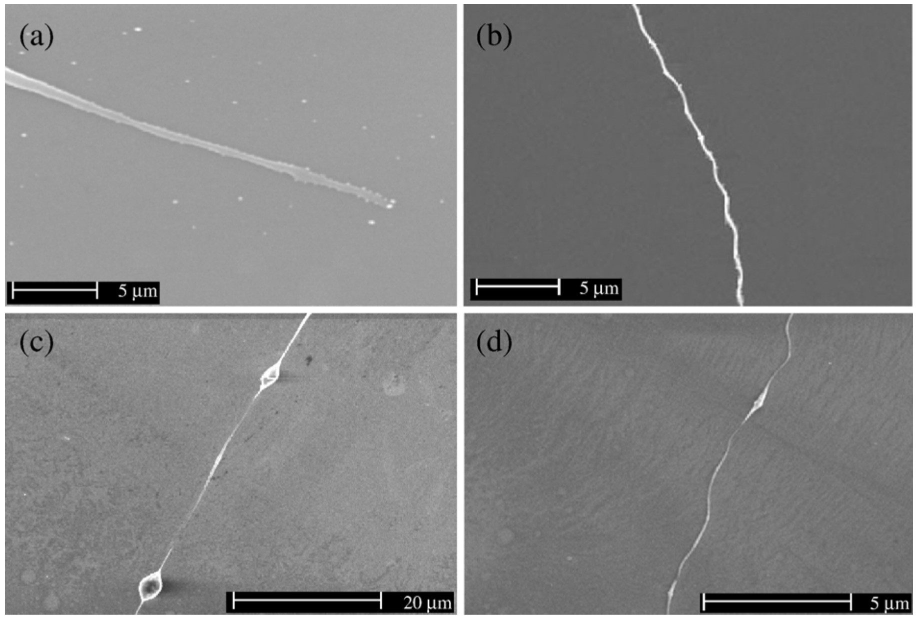

Fig. 3. SEM images of fibers prepared via ANES using different parameters: (a) a spinning voltage of 10 V and a spinning distance of 10 μm; (b) a spinning voltage of 10 V and a spinning distance of 15 μm; (c) a spinning voltage of 10 V and a spinning distance of 20 μm; (d) SEM image of fiber formed by ANES at a spinning voltage of 12 V and a spinning distance of 20 μm.

20 μm, the electric field strength is 0.6 V/ μm and a single fiber with an average diameter of 123 ± 15 nm can be produced as shown in Fig. 3(d). This is due to the increased field strength that sufficiently stretches the solution to form a relatively smooth microstructure.

It is evident from the experiments that the spinning distance has an influence on the formation of fibers prepared using ANES, since the variation of the spinning distance affects the strength of the electrostatic field that initiates the ANES process. In other work done by our group, current is monitored during local anodic oxidation of silicon using an AFM and used to provide for in situ quality control during nanolithography [19]. It is hypothesized that similar techniques can be used to potentially control fiber formation during electrospinning. In the experiments, the minimal applied electric field required to start the ANES process is around 0.6 V/ μm. The experiments also show that the applied voltage not only affects the strength of the electric field but also influences the ANES process. With the same electric field strength, a high applied voltage appears to initiate the ANES process more easily. This is because the atomization and cone-jet formation is determined by both the electric field and the charge density on the surface of solution droplets. The research demonstrated that voltage and spinning distance do not significantly affect the diameter of the electrospun fibers when the electric field strength was fixed. For instance, a short distance and low voltage could also generate similar electrospun fibers as ones produced using long distances and larger spinning voltages due to similar electric field strengths [11, 20]. The translational speed of the stage in the electrospinning process can affect the patterns of the deposited electrospun fibers, but it will not influence the geometry of the nanofibers, which is affected determined by the electric field strength [21]. The ANES process can be considered a promising technique to generate one-dimensional materials at the nanoscale. Eventually, this technique will be further developed into an innovative and versatile process for manufacturing by combining simultaneous synthesis and assembly of one-dimensional nanoscale materials onto nano-and microscale devices.

The following advantages of a fully-developed ANES technique are apparent: (1) it is a one-step process to fabricate and integrate nanofibers on predetermined areas, eliminating some intermediate steps of classical electrospinning. Therefore, it has shorter processing time and is more cost-effective; (2) a micrometer sized AFM tip is used in ANES but it is still easy to obtain nanometer fibers; (3) nanofibers prepared via ANES can be manipulated on a substrate with nanometer resolution as a result of the AFM's precisely controllable nanoscale translational stages; (4) the integration of nanofibers within nano-scale devices will be relatively easy to control; device fabrication is well controlled through a computer-controlled and automated AFM design platform; (5) comparison with other methods for preparing nanofibers, such as chemical vapor deposition and self-assembly, renders ANES an inexpensive technique with potential to control the diameters of fibers through variations of electrospinning parameters [22]; (6) the precursor can be easily changed to supply different materials to the AFM tip which makes ANES capable of multi-compound materials fabrication; and (7) the voltage bias for ANES is relatively low; ~ 10 V with a separation distance of ~ 10 μm, compared to other electrospinning techniques and thus will not change or damage the chemical and physical properties of the electrospun polymer nanofibers [23].

4. Conclusions and further work

ANES is a process by which nanometer fibers are created from a viscous polymer solution by applying an electric field to a droplet of the solution coated on an AFM tip. This preliminary investigation demonstrates the feasibility of preparing single nanofibers using an AFM tip in a controllable fashion. ANES is an innovative nanofabrication method geared towards precise nano-scale fiber generation. We envisage further study showing ANES developed into a multifunctional manufacturing tool through in situ production, process control, and imaging. Nanofibers

produced in such a controllable way would be useful for the heterogeneous integration of nanofibers within bio-nanotechnological systems using biofunctional polymer materials.

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