

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230965355>

A scanning tip electrospinning source for deposition of oriented nanofibres

Article in *Nanotechnology* · September 2003

DOI: 10.1088/0957-4484/14/10/310

CITATIONS

182

READS

453

7 authors, including:



Jun Kameoka

Texas A&M University

108 PUBLICATIONS 2,760 CITATIONS

[SEE PROFILE](#)



Yanou Yang

Bristol-Myers Squibb

15 PUBLICATIONS 587 CITATIONS

[SEE PROFILE](#)



David Czaplewski

Argonne National Laboratory

128 PUBLICATIONS 4,078 CITATIONS

[SEE PROFILE](#)



Geoffrey Coates

Cornell University

294 PUBLICATIONS 21,540 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Single molecular detection [View project](#)



Renewable Energy, Green Energy, Blue Energy, Ocean Wave Energy Harvesting [View project](#)

A scanning tip electrospinning source for deposition of oriented nanofibres

Jun Kameoka¹, Reid Orth¹, Yanou Yang¹, David Czaplewski¹,
Robert Mathers², Geoffrey W Coates² and H G Craighead¹

¹ School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853, USA

² Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

Received 21 March 2003, in final form 17 June 2003

Published 5 September 2003

Online at stacks.iop.org/Nano/14/1124

Abstract

We present a method for controlled deposition of oriented polymeric nanofibres. The method uses a microfabricated scanned tip as an electrospinning source. The tip is dipped in a polymer solution to gather a droplet as a source material. A voltage applied to the tip causes the formation of a Taylor cone, and at sufficiently high voltages, a polymer jet is extracted from the droplet. By moving the source relative to a surface, acting as a counter-electrode, oriented nanofibres can be deposited and integrated with microfabricated surface structures. For example, we deposited fibres of polyethylene oxide with diameters ranging from 100 to 1800 nm, with the diameter primarily depending on the concentration of the polymeric solution. In addition to the uniform fibre deposition, the scanning tip electrospinning source can produce self-assembled composite fibres of micro- and nanoparticles aligned in a polymeric fibre. We also deposited oriented conductive polymeric fibres of polyaniline and investigated the conductivity of these fibres as components for polymeric nanoelectronics.

1. Introduction

Electrospinning has been used to fabricate randomly oriented polymeric fibres [1–16]. In the conventional approach, a syringe with a diameter typically of 0.3–1 mm has been used as an electrospinning source [1–16], with a pendant droplet of polymeric solution formed at the end of the tubing. In this process, a high voltage applied between the droplet and a counter-electrode establishes a Taylor cone and extracts a liquid jet. The extracted jet dries to form a fibre on the counter-electrode. The distance between the droplet and the counter-electrode was conventionally 5–25 cm. The typical electric field applied for these processes was 1000–3000 V cm⁻¹. A variety of polymeric nanofibres have been electrospun by this syringe fabrication method, such as a silk-like polymer with fibronectin (SLPF) [4], polyethylene [9, 10], polylactide (PLA) [12] and random copolymers [13]. In addition to polymers, composite materials have been electrospun recently [14]. There are several publications that describe the possible applications that can take advantage of the size or the high surface to volume ratio of the fibres, including

membranes, filters, drug delivery, composites and biomimetic materials [15, 16].

The fabrication of oriented and single nanofibres, rather than random configurations, is of great interest for molecular electronics applications. In addition to the orientation, the integration of nanofibres with microfabricated structures, such as electrodes, used for carbon nanotubes or nanowire is necessary [17–23]. A deposition system to orient nanofibres electrospun on the edge of a rotating tapered wheel-like bobbin has been reported [11]. Conductive nanofibre films have been fabricated by electrospinning polyaniline doped with camphorsulfonic acid (Pan HCSA) [5]. The conventional electrospinning system does not allow integration of individual nanofibres with microfabricated structures, such as electrodes or surface morphologies. Our approach using the fabricated tip does permit this integration.

We have used a triangle electrospray emitter tip integrated with a microfluidic device and interfaced to a mass spectrometer [24]. The triangular tip acts like a nozzle that helps the liquid to establish a Taylor cone. This device was also used to fabricate nanofibres that can be integrated with

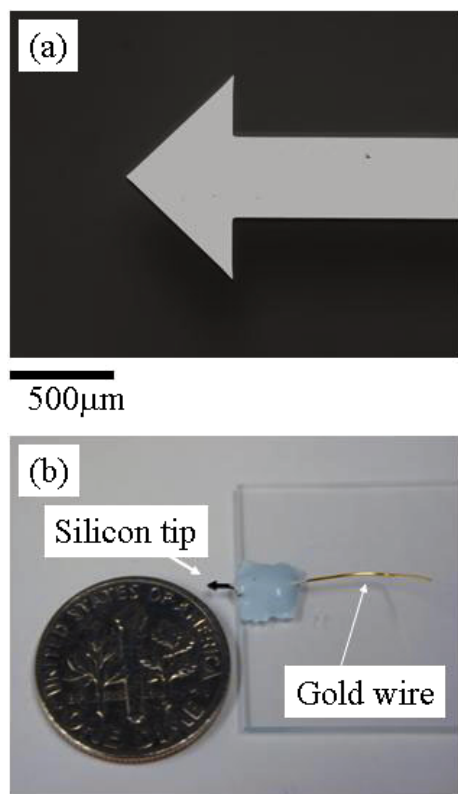


Figure 1. (a) Optical image of a silicon scanning tip. (b) Scanning tip mounted on a glass substrate electrically connected with a gold wire.

microfabricated structures [25]. We have used the feature of a microfabricated tip in this scanning tip approach.

In this paper, we describe a new technique for oriented polymeric nanofibres, using a microfabricated silicon tip as a scanning source. This approach allows nanofibre integration with microfabricated structures. The scanned tip electrospinning deposition (STED) technique can deposit functional polymeric nanostructures without the need for lithography and without the limitation of processes in which a scanning tip contacts a surface. The deposited fibre can be a functional element such as a conducting polymer or it can be used as a medium for self-assembled deposition of other elements such as particles or nanodevices contained in the solution.

2. Tip fabrication and sample preparation

The silicon tip was formed by conventional silicon fabrication processes. A 3 µm silicon dioxide layer was deposited on a silicon wafer. A 10 µm layer of Shipley 1075 photoresist was coated on the silicon dioxide and patterned using contact lithography. The photoresist was developed and the silicon dioxide layer was etched by CHF_3/O_2 reactive ion etching using the photoresist as a mask. The silicon oxide layer was used as a mask for Bosch etching to pattern arrow-shaped tips on a wafer by etching entirely through the wafer. After the etching process, the silicon dioxide layer was removed by wet etching in hydrofluoric acid. As a final step, gold was deposited on the surface of the etched wafer to increase the conductivity

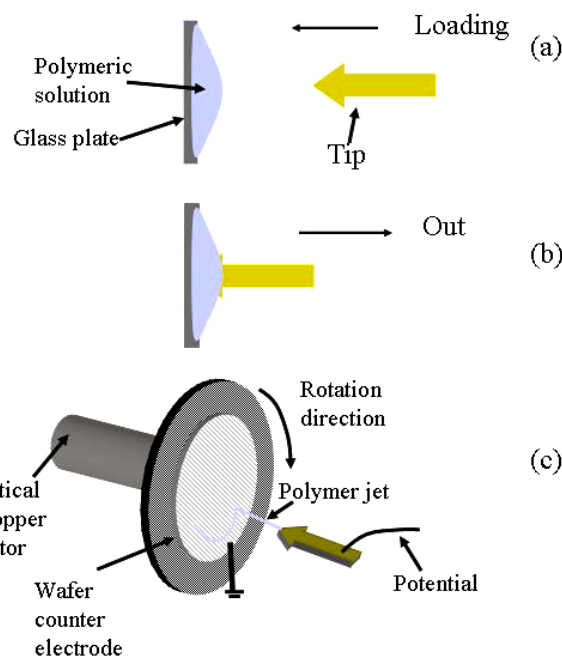


Figure 2. Polymeric nanofibre fabrication process. (a) Scanning tip was dipped in a polymeric solution. (b) Scanning tip was taken out of the polymeric solution and a liquid droplet was formed on the scanning tip. (c) The potential was applied to a gold wire connected to the scanning tip and the liquid jet was extracted. The fibre jet was deposited on a counter electrode that was attached to an optical chopper motor for controlling nanofibre orientation.

of the tips. We fabricated an array of 25 tips on one wafer, which we cleaved apart for individual use. Figure 1(a) shows an optical micrograph of an arrow-shaped tip. This tip was connected to a gold wire by which the extraction voltage was applied. An optical micrograph of a whole device is shown in figure 1(b).

The schematic diagram of the nanofibre fabrication process is shown in figure 2. As a first step, the arrow tip was dipped in a polymeric solution to acquire a droplet and then removed (figures 2(a) and (b)). The arrow shape of the tip helped to establish a droplet localized on the tip. For observation of the spraying process, the tip with the droplet was placed 2 cm from the counter-electrode to allow enough clearance to observe the Taylor cone on the tip through a stereomicroscope (figure 2(c)). To minimize the effect of liquid evaporation from the droplet, the deposition was done a few seconds after the droplet formation by applying a potential of 4000–6000 V between the tip and the substrate. For the aligned fibre deposition, the counter-electrode was attached to an optical chopper motor that provided a simple means to control the motion of the tip relative to the substrate by adjusting the velocity of the motor (figure 2(c)). Clearly, other scanning approaches could be used to make patterns of various shapes.

The polyethylene oxide (PEO) polymer solution was prepared by dissolving PEO polymer ($M_w \sim 100\,000$, purchased from Acros Organics NJ, USA) in weight concentrations of 5, 10, 20 and 30% in a solvent of 50% deionized water and 50% ethanol. For composite particle deposition, a 50–50 mixture of the 20% PEO polymer

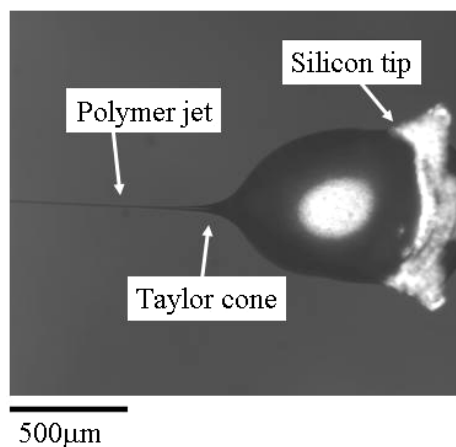


Figure 3. Optical image of polymer liquid jet extracted from an apex of a Taylor cone established on a silicon tip.

solution and a fluorescent latex nanosphere suspension was prepared. The final approximated PEO polymer weight concentration in the prepared polymeric colloidal solutions was 10%. The diameters of the fluorescent latex spheres used in this experiment were 100 and 500 nm, with a concentration of latex nanospheres of 9.0×10^{11} and 7.0×10^{11} particles ml^{-1} respectively. Polyaniline (PANI) (48 mg, emeraldine base; $M_w \sim 20\,000$, purchased from Aldrich, WI, USA) was dissolved in chloroform (1.5 ml) and doped with 10-camphorsulfonic acid (122 mg). PEO (48 mg, $M_w \sim 900\,000$, purchased from Aldrich, WI, USA) was added to the chloroform solution and stirred overnight. The concentration of PEO/PANI-HCSA ranged from 0.5 to 2.0 wt%. The amount of PEO mixed with PA varied from 10 to 80 wt%.

3. Results and discussion

The scanning source was used to fabricate oriented nanofibres and integrate single nanofibres with microfabricated structures such as trenches or electrodes. The configuration of nanofibres integrated with surface features was critical to fabricate nanofibre-based nanodevices. The operation of our source is quick and straightforward; therefore, this scanning system is suitable for rapid fabrication of nanofibre based devices.

An optical micrograph of a Taylor cone and a polymeric jet, established with 4500 V applied to a $20\ \mu\text{l}$ droplet and the counter-electrode, is shown in figure 3. Nanofibres were deposited for 5–10 s, while the Taylor cone was observed. The length of the nanofibre is controlled by the volume of droplet loaded on the tip. The nanofibres were deposited within a 5 mm spot. To reduce the effects of liquid evaporation, the deposition process was initiated immediately after the polymeric solution was loaded. In addition to the arrow-shaped tip, we also tested triangle-shaped and a straight metal wire tip. It was found that it was more difficult to form a Taylor cone at the end of metal wire tips.

We have investigated the performance of this microfabricated tip by electrospinning PEO polymer solutions with low to high concentration without scanning. Figures 4(a)–(d) show scanning electron micrographs of nanofibres electrospayed from a 5, 10, 20 and 30% PEO polymer solutions. The diameters of nanofibres deposited from the various solutions were in the 100–200 nm range for 5%, the 200–300 nm range for 10%, the 300–500 nm range for 20% and the 500–1800 nm range for 30%. The polymer viscosity increased with concentration. The viscosity of 30% polymeric solution was very high and it was difficult to pump and electrospun through a syringe. From these results, we concluded that the diameter

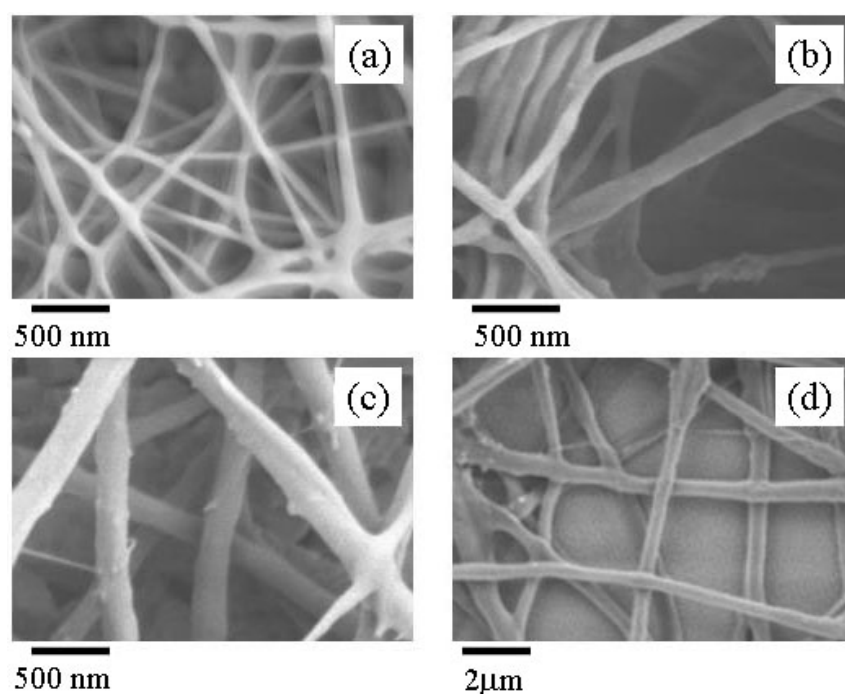


Figure 4. Polyethylene oxide nanofibre fabricated by electrospaying from a (a) 5% PEO solution, (b) 10% PEO solution, (c) 20% PEO solution, (d) 30% PEO solution.

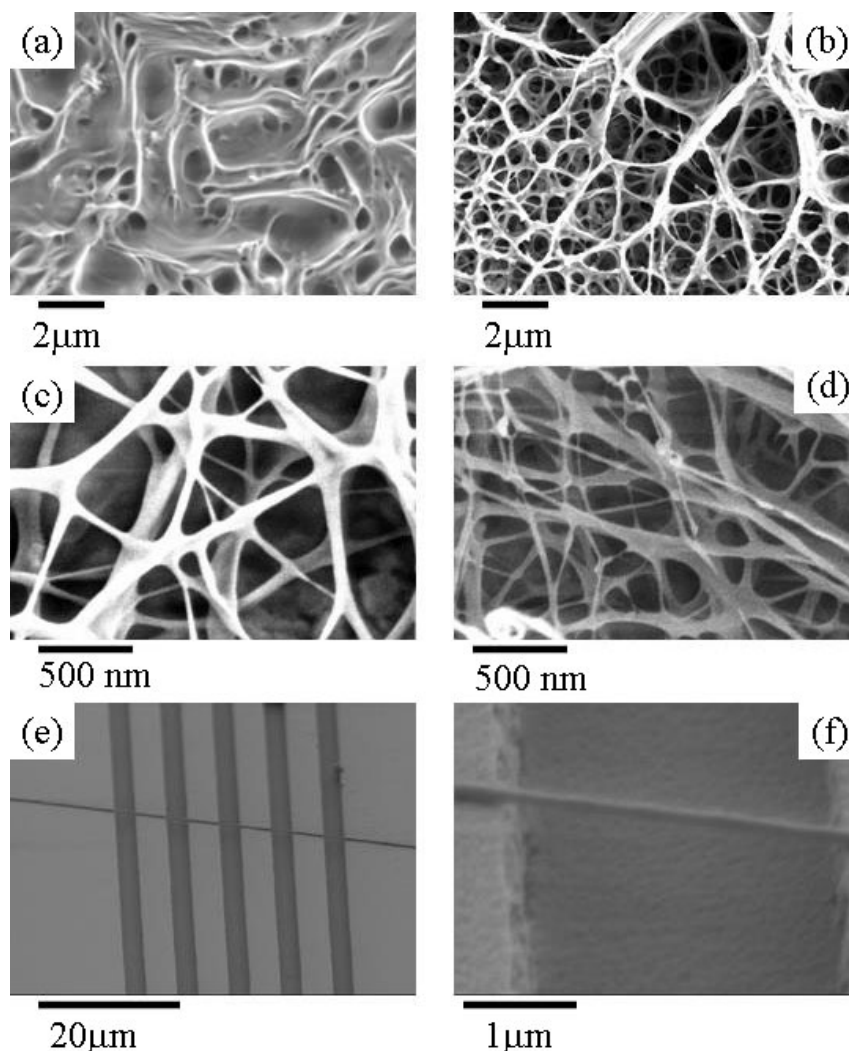


Figure 5. Polyethylene oxide nanofibre fabricated by electrospinning 10% PEO solution with varying deposition distance: (a) 0.5 cm deposition distance, (b) 0.75 cm deposition distance, (c) 1.0 cm deposition distance, (d) smallest nanofibre fabricated from 5% PEO solution; the diameter is about 45 nm. (e) Scanning electron micrograph of suspended and oriented nanofibres. PEO nanofibres over a 3 μm wide trench. (f) Magnified image of figure 5(e).

of nanofibres depended on the concentration of polymeric solution, with thicker fibres fabricated from polymeric solution with higher concentration. This result is consistent with the conventional approach of syringe needle electrospinning. The final diameter of nanofibre, deposited on the counter-electrode, depends on the initial diameter of liquid jet which is influenced by viscosity, with lower-viscosity solutions producing thinner fibres [4]. However, to the best of our knowledge, this is the first time that the electrospinning from a highly viscous polymeric solution has been demonstrated to fabricate nanofibres with diameters greater than 1.5 μm .

In addition to investigating the influence of polymer concentration on the nanofibre diameter, we investigated the influence of the deposition distance on the nanofibre diameter. As the deposition distance was changed from 0.5 to 1.5 cm, changes were observed in the nanofibre morphology. In the case of the 0.5 cm deposition distance, the scanning electron micrograph of nanofibres, fabricated on the counter-electrode, is shown in figure 5(a). The deposited polymer

resembled a membrane. We expect this to be the result of the small deposition distance and short transit distance that causes the polymer solution to arrive at the electrode as a wet polymer. In the case of the 0.75 cm deposition distance, the scanning electron micrograph of nanofibres fabricated on the counter-electrode under these conditions is shown in figure 5(b). In this case, cylindrical nanofibres were formed with an average diameter of 408 nm (200–850 nm range). The nanofibres appear to have partially dried while travelling to the counter-electrode. The scanning electron microscope image of nanofibres with 1.0 cm deposition distance is shown in figure 5(c). Thinner nanofibres were formed in this case with an average diameter of 153 nm. If the deposition distance is more than 1.0 cm, cylindrical nanofibres are fabricated. For shorter source–substrate distances, the spun fibres arrive at the surface before the solvents are fully evaporated. The fibres can then merge to form larger fibres or bond together to make a fibrous web. It appears that once the fibres form in transit, the nanofibre diameter is fixed and the fibres are deposited on the surface as a solid. The smallest diameter of random nanofibres

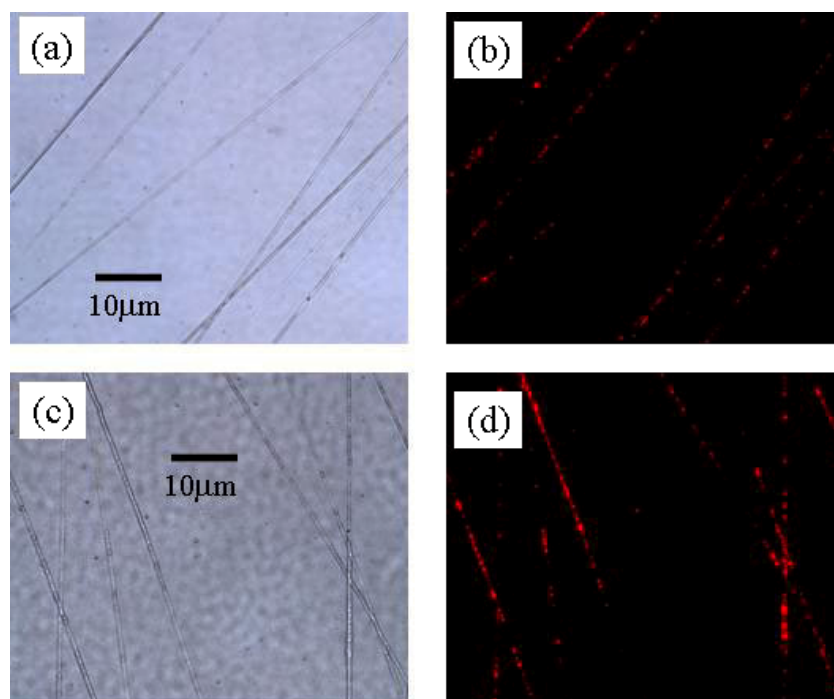


Figure 6. Latex fluorescent nanospheres confined in a polyethylene oxide nanofibre. (a) A bright field image of PEO nanofibres with 100 nm nanospheres. (b) Fluorescent image of figure 6(a). (c) A bright field image of PEO nanofibres with 500 nm nanospheres. (d) Fluorescent image of figure 6(c).

fabricated with this solution concentration was about 45 nm, which is shown in figure 5(d).

The STED technique was also used to fabricate suspended and orientated nanofibres and integrate them with microfabricated structures. The motion of the tip relative to the substrate was used to control the nanofibre orientation. The linear velocity of an optical chopper motor was 168 cm s^{-1} for all experiments at the deposition site on the counter-electrode. Utilizing a linear velocity less than 168 cm s^{-1} produced slightly bent nanofibres, instead of completely straightened nanofibres. Linear velocity faster than 168 cm s^{-1} produced fully straightened nanofibres. A liquid jet extracted from the Taylor cone was deposited over the microfabricated gap on a counter-electrode. Figure 5(e) shows an orientated PEO nanofibre suspended over a $3 \mu\text{m}$ wide trench by electrospinning a 10% PEO solution. Figure 5(f) shows a magnified nanofibre over the one of trenches shown in figure 5(e).

We have also investigated the capability of the STED technique for depositing composite materials by electrospaying of a mixture of PEO and colloidal particles. The mixture of PEO solution and fluorescent nanospheres with 100 and 500 nm diameters were prepared and electrospun from the scanned tip. The rotation of the optical chopper motor was used to control the nanofibre orientation. Figure 6(a) shows a bright field image of nanofibres with 100 nm diameter latex nanospheres fabricated. Nanofibres were straightened with about 30° variation along the rotational direction rather than in a random configuration. Figure 6(b) is a fluorescent image of figure 6(a). Latex nanospheres were confined in nanofibres and self-assembled along the nanofibres. The diameter of these nanofibres was in the 100–300 nm range. The line density of the nanospheres confined in the nanofibres was

$0.75 \text{ particles } \mu\text{m}^{-1}$. Figure 6(c) shows a bright field image of nanofibres electrospun from PEO solution with 500 nm latex nanospheres. Figure 6(d) is a fluorescent image of figure 6(c). 500 nm latex nanospheres were confined in nanofibres, the diameter of the PEO nanofibre was about 100–300 nm range. The line density of nanospheres confined in these nanofibres was $0.68 \text{ particles } \mu\text{m}^{-1}$. The STED technique was also used to fabricate orientated composite nanofibres integrated with a microfabricated structure.

We have also demonstrated the integration of conductive fibre with a four-point electrode using the STED system. A single fibre made from a blend of PEO and PANI solutions was deposited on the four electrodes, which was fabricated on a silicon wafer coated with a thin layer of SiO_2 . A scanning electron micrograph of the fibre integrated with four electrodes is shown in figure 7(a). The diameter of this fibre is about $1.5 \mu\text{m}$. A current/voltage (I/V) curve is obtained by a standard four-probe measurement and shown in figure 7(b). The conductivity of this single fibre is $\sim 0.01 \text{ S cm}^{-1}$ calculated from the graph and figure 7(a).

The STED process to fabricate nanofibres takes only one minute due to the simple polymer solution loading process. The conventional syringe deposition system requires some time because loading the polymeric solution into the syringe and connecting the syringe to the pumping equipment takes several minutes. In the case of multiple sample spinning, it is obvious that the STED is much quicker than that of syringe deposition system. In addition to the high fabrication efficiency, scanned tips are economical because more than 100 tips can be made on one silicon wafer and they can be reused after surface cleaning. Because the microfabricated tip does not have a tube to supply a polymeric

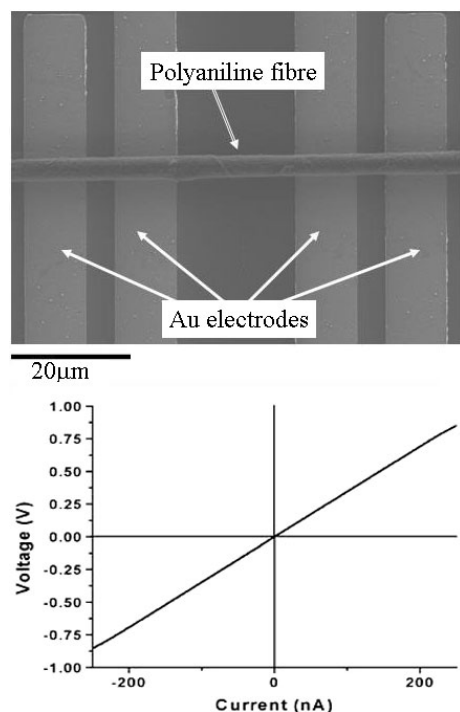


Figure 7. Characterization of conductive polymer fibre made from PEO and PANI. (a) The scanning electron micrograph of fibre integrated with four electrodes. (b) I/V curve of the fibre. The linear curve was fit to the data.

solution, a wide range of polymeric material, especially highly viscous polymeric solutions, can be electrospun from the tip. Comparatively, it is difficult to pump highly viscous polymeric solution through the syringe. Another advantage of the scanned tip is the easy control of the orientation of nanofibres and the integration with microfabricated structures due to the short deposition distance. The deposition distance of the syringe system is usually more than 10 cm and our system only requires 2 cm. We also showed the capability of electrospinning a colloidal suspension mixed with a polymer solution to fabricate nanofibre composite materials using the STED system. In addition to the formation of nanofibres, the scanning electrospray may be used as a method of liquid, chemical or particulate deposition on a surface.

4. Conclusion

We have demonstrated nanofibre fabrication using a STED. This electrospinning deposition source does not require a nozzle; therefore, a highly viscous polymeric solution could be electrospun to form a thick nanofibre. The volume required for the deposition was very small and the system operation was simple and quick. Therefore, this deposition system is suitable for rapid nanofibre deposition from different materials for analysis or to make more complex structures. We also demonstrated that latex beads were confined in orientated nanofibres electrospun from a mixed solution of PEO and a

latex nanosphere suspension. This approach can allow the fabrication of self assembled one-dimensional wires. The scanned electrospinning deposition system can also provide a method to integrate nanofibres with microfabricated structures. Orientated and suspended nanofibres were fabricated, which may open a new field of nanofibre-based electronics and sensors. The deposition could possibly be more controlled by utilizing electrostatic focusing.

Acknowledgments

This work was supported by the Nanobiotechnology Center (NBTC), an STC Program of the National Science Foundation under Agreement No ECS-9876771. The authors appreciate access and use of the Cornell Nanofabrication Facility located at Cornell University.

References

- [1] Doshi J and Reneker D H 1995 *J. Electrostat.* **35** 151
- [2] Shin Y M, Hohman M M, Brenner M P and Rutledge G C 2001 *Appl. Phys. Lett.* **78** 1149
- [3] Deitzel J M, Kleinmeyer J D, Hirvonen J K and Beck Tan N C 2001 *Polymer* **42** 8163
- [4] Buchko C J, Chen L C, Shen Y and Martin D C 1999 *Polymer* **40** 7397
- [5] Norris I D, Shaker M M, Ko F K and MacDiarmid A G 2000 *Synth. Met.* **114** 109
- [6] Reneker D H and Chun I 1996 *Nanotechnology* **7** 216
- [7] Fong H and Reneker D H 1999 *J. Polym. Sci. B* **37** 3488
- [8] Reneker D H, Yarin A L, Fong H and Koombhongse S 2000 *J. Appl. Phys.* **87** 4531
- [9] Fong H and Reneker D H 1999 *Polymer* **40** 4585
- [10] Koombhongse S, Liu W and Reneker D H 2001 *J. Polym. Sci. B* **39** 2598
- [11] Theron A, Zussman E and Yarin A L 2001 *Nanotechnology* **12** 384
- [12] Bogwitzki M, Frese T, Steinhart M, Greiner A and Wendorff J 2001 *Polym. Eng. Sci.* **41** 982–9
- [13] Deitzel J M, Kleinmeyer J D, Hirvonen J K, Beck Tan N C, DeSimone J M and Crette S 2002 *Polymer* **43** 1025
- [14] Shao C, Kim H, Gong J and Lee D 2002 *Nanotechnology* **13** 635
- [15] Gibson P W, Schreuder-Gibson H L and Riven D 1999 *AIChE J.* **45** 190
- [16] Katti D S, Robinson K W, Attawia M A, Ko F K and Laurencin C T 2002 *Society for Biomaterials 28th Annual Mtg Transactions* p 143
- [17] Liu L, Jayanthi C S, Tang M, Wu S Y, Tomblor T W, Zhou C, Alexseyev L, Kong J and Dai H 2000 *Phys. Rev. Lett.* **84** 4950
- [18] Walters D A, Ericson L M, Casavant M J, Liu J, Colbert D T, Smith K A and Smalley R E 1999 *Appl. Phys. Lett.* **74** 3803
- [19] Zhang Y and Dai H 2000 *Appl. Phys. Lett.* **77** 3015
- [20] Kim L, Gu G, Waizmann U and Roth S 2002 *Appl. Phys. Lett.* **80** 1815
- [21] Duan X, Huang Y, Cui Y, Wang J and Lieber C M 2001 *Nature* **409** 66
- [22] Huang Y, Duan X, Wei Q and Lieber C M 2001 *Science* **291** 630
- [23] Cui Y and Lieber C M 2001 *Science* **291** 851
- [24] Kameoka J, Orth R, Ilic B, Czaplewski D, Wachs T and Craighead H G 2002 *Anal. Chem.* **74** 5897
- [25] Kameoka J and Craighead H G 2003 *Appl. Phys. Lett.* **83** 372