

Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Nanoscale

ARTICLE

Patterned, highly stretchable and conductive nanofibrous PANI/PVDF strain sensors based on electrospinning and *in situ* polymerization

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gui-Feng Yu^{a),b)†}, Xu Yan^{a)†}, Miao Yu^{a),c)†}, Meng-Yang Jia^{d)}, Wei Pan^{a),e)}, Xiao-Xiao He^{a)}, Wen-Peng Han^{a)}, Zhi-Ming Zhang^{d)†}, Liang-Min Yu^{d)}, and Yun-Ze Long^{a),f)*}

A facile fabrication strategy via electrospinning and followed *in situ* polymerization to fabricate patterned, highly stretchable, and conductive polyaniline / poly(vinylidene fluoride) (PANI/PVDF) nanofibrous membrane is reported. Owing to the patterned structure, the nanofibrous PANI/PVDF strain sensor can detect a strain up to 110%, for comparison, which is 2.6 times higher than the common nonwoven PANI/PVDF mat and much larger than previously reported values (usually less than 15%). Meanwhile, the conductivity of patterned strain sensor shows a linear response to the applied strain in a wide range from 0% to about 85%. Additionally, the patterned PANI/PVDF strain sensor can completely recover to its original electrical and mechanical values within a strain range of more than 22%, and exhibits good durability over 10,000 folding-unfolding tests. Furthermore, the strain sensor also can be used to detect finger motion. The results demonstrate promising application of the patterned nanofibrous membrane in flexible electronic fields.

1. Introduction

Nanofibrous membranes have aroused considerable attention due to their tunable physical/chemical properties, light weight, low cost, high surface to volume ratio, variable pore-size distribution and high porosity. Various methods such as ultrasonic irradiation synthesis,¹ nanoprinting,² dielectrophoresis synthesis,³ template-free method,⁴ electrospinning,⁵ etc. have been introduced to fabricate nanofibers. Among the methods mentioned above, electrospinning is a simple, cost-efficient and highly versatile method to generate randomly arranged nonwoven membranes. However, precisely positioning individual nanofibers, e.g. patterned fibrous membrane is very useful in many fields, such as microelectronic and photonic devices,^{6,7} artificial tissue scaffolds and drug delivery system.⁸⁻¹⁸ Furthermore, owing to the random fiber orientation of nonwoven membrane, some features and applications are limited. For example, the sensor made of poly(3,4-

ethylenedioxythiophene) : poly(styrene sulfonate) - poly(vinyl alcohol) (PEDOT:PSS-PVA) as-spun nanofibrous membranes could only bear a small strain of 1.2%,^{19,20} electrospun PVDF nonwoven membrane coated with poly(vinylidene fluoride) (PPY) could endure a strain of 2.8%,²¹ and electrospun PVDF nonwoven mat coated with PANI could withstand a larger strain up to 14.5%.²²

On the other hand, three main methods have been developed to control the pattern of the nanofibrous membrane by changing the configuration^{8,9} or surface architectures¹³⁻¹⁸ of the collectors, post-processing treatment of the as-spun membranes,^{10,11} and near-field electrospinning.¹² Among them, using a collector with special architectures^{5,8-18} is the most simple and effective method. Nevertheless, previous studies are mainly focused on two aspects of the patterned membranes. One is the formation mechanism of patterned structures via electrospinning, which can be attributed to the redistribution of static electric field.¹⁷ Another is the biomedical application of patterned nanofibrous membranes,⁸⁻¹⁸ because of the similarity in structural geometries between electrospun nanofibrous scaffolds with those of natural extracellular matrix found in human body. However, patterned nanofibrous membranes with good electrical and mechanical properties have rarely been reported, which may be used in cutting-edge flexible/stretchable electronics.

In this paper, we introduce a new type of stretchable conductive strain sensor based on patterned nanofibrous PANI/PVDF membrane. Thanks to the constituent and fabricating method, the patterned PANI/PVDF membrane collected by a metal grid can measure and withstand a maximum strain up to 110 %,

^a Collaborative Innovation Center for Nanomaterials & Optoelectronic Devices, College of Physics, Qingdao University, Qingdao 266071, P. R. China. E-mail: yunze.long@163.com or yunze.long@qdu.edu.cn

^b College of Science & Information, Qingdao Agricultural University, Qingdao 266109, P. R. China

^c Department of Mechanical Engineering, Columbia University, New York, 10027, USA

^d Key Laboratory of Marine Chemistry Theory & Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China. E-mail: zmcyj@ouc.edu.cn

^e College of Chemistry & Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, China

^f Collaborative Innovation Center for Marine Biomass Fibers, Materials & Textiles of Shandong Province, Qingdao University, Qingdao 266071, P. R. China

[†]These authors contributed to this work equally.

which is 2.6 times higher than its counterpart (common nonwoven membrane). Additionally, it can recover to the original mechanical and electrical values even under a large strain of 22%. In addition, the patterned PANI/PVDF sensor also has high durability and stability (10,000 cycles at bending) and high sensitivity. Meanwhile, tapping and finger motion sensing are measured by using the patterned PANI/PVDF sensor. These important features (high stretchability, elasticability, repeatability, durability, stability and sensitivity) allow the material to be used in flexible sensors.

2. Experimental

2.1 Preparation of patterned PVDF membrane (Fig. 1A)

Fig. 1 illustrates the schematic depiction of the process in fabricating a PANI/PVDF nanomembrane sensor. This fabrication process is simple, scalable, and economic. At first, patterned PVDF thin membranes were obtained by electrospinning. In the process, PVDF was dissolved in N,N-dimethylformamide (DMF) and acetone (1:1) to form a 22 wt% electrospinning precursor, then a high-voltage DC power supply (DW-P303-1ACFO, Tianjin Dongwen) was used to produce voltage of 10 kV, and the distance from the spinneret to collector was about 8 cm. The first kind of collector is the electrical conductive collector with different patterned architectures, such as sexangle-patterned collector (Fig. 2a), nearly rectangle-patterned collector (Fig. 2b), metal grid collector (Fig. 2c) and circular patterned collector (Fig. 2d). Moreover, it was observed that the obtained PVDF membrane had the similar shape and dimension of the configuration of the patterned collectors, namely, uniaxial parallel nanofiber aligning on the electrical wires and random orthogonal arrangement in the spacing between the wires,^{17,18} as shown in Fig. 2. For comparison, a flat aluminum foil as collector was introduced, as we know, a common nonwoven nanomembrane was obtained. All experiments were carried out at ambient humidity (about 45 RH%).

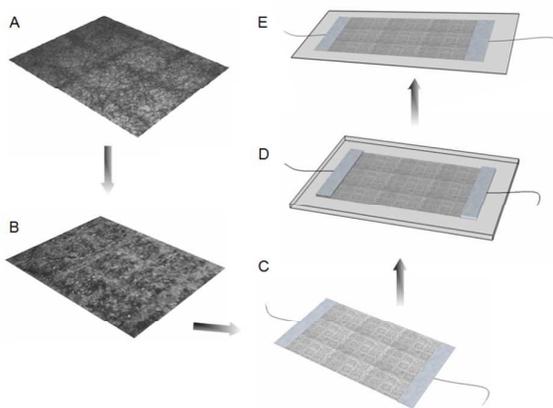


Fig. 1. Schematic of the fabrication process of patterned PANI/PVDF sensor. (A) Electrospinning of patterned PVDF membrane. (B) *In situ* polymerization of PANI on the patterned nanofibrous PVDF membrane. (C) Fabrication of sensor electrodes. (D) Patterned sensor sandwiched by PDMS membranes. (E) Sensing property measurements under different strains.

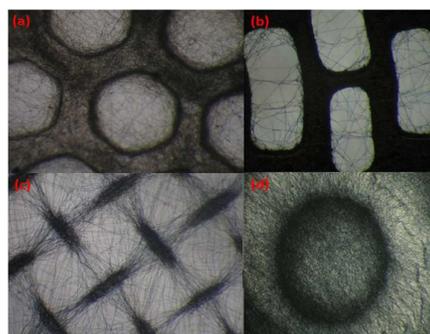


Fig. 2. Optical image of the patterned membranes obtained from different collectors.

2.2 Synthesis of PANI /PVDF patterned nanomembrane (Fig. 1B)

At first, 4.60 g ammonium persulphate (APS) was dissolved adequately in 50 ml deionized water to make up solution I. Secondly, 1.875 g aniline and 2.54 g sulfosalicylic acid (SSA) were added into 50 ml deionized water to form solution II. Then the patterned PVDF membrane was immersed in the blended solution of I and II. After that, the obtained mixture was kept steady at room temperature for 12 h. With chemical oxidative polymerization of PANI, the solution underwent a color change from light yellow to deep green.²³ For comparison, the membrane (PVDF) underwent a color change of white to deep green (PANI/PVDF). After washing the impurities with deionized water and drying at room temperature, a patterned PANI/PVDF membrane with different patterns was obtained finally.

2.3 Sensor assembly

To assemble a strain sensor, two copper wires with a distance of 9.5 mm were fixed on the nanofibrous PANI/PVDF membrane by silver paste as sensor electrodes (Fig. 1C), and then PDMS (Dow Corning Sylgard184; ratio of base to crosslinker, 10:1 by mass) thin layer was mixed, degassed and poured against the two surfaces of the membranes to package the device (Fig. 1D).

2.4 Sensing property measurements

The resultant fibrous PVDF and PANI/PVDF membranes (Fig. 3a) were characterized by an optical microscope (Olympus-BX51). The photograph shows that the collector pattern is mimicked by the electrospun membrane well, as shown in Fig. 3b. Figs. 3c-d exhibit the SEM images of the fibrous PVDF and PANI/PVDF membranes, separately. Both the current-voltage (I-V) characteristics without stretching (Fig. 1D) and under different strains (Fig. 1E) were measured by a Keithley 6487 high resistance meter system and a home-made stretching device at room temperature.²⁰

3. Results and discussion

3.1 Stretchability test

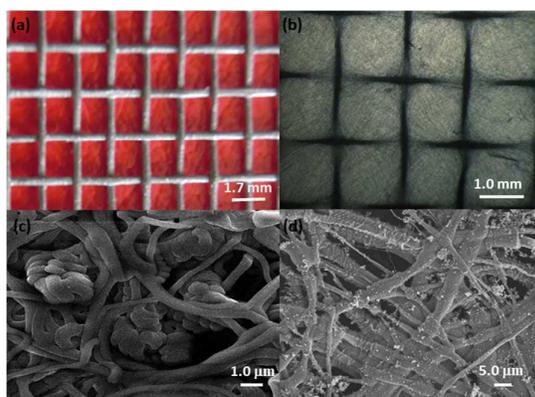


Fig. 3. (a) Optical image of the patterned metal-grid-collector; (b) Optical image of the electrospun patterned PVDF membrane after removing the patterned collector; SEM images of the fibrous PVDF (c) and PANI/PVDF (d) membranes.

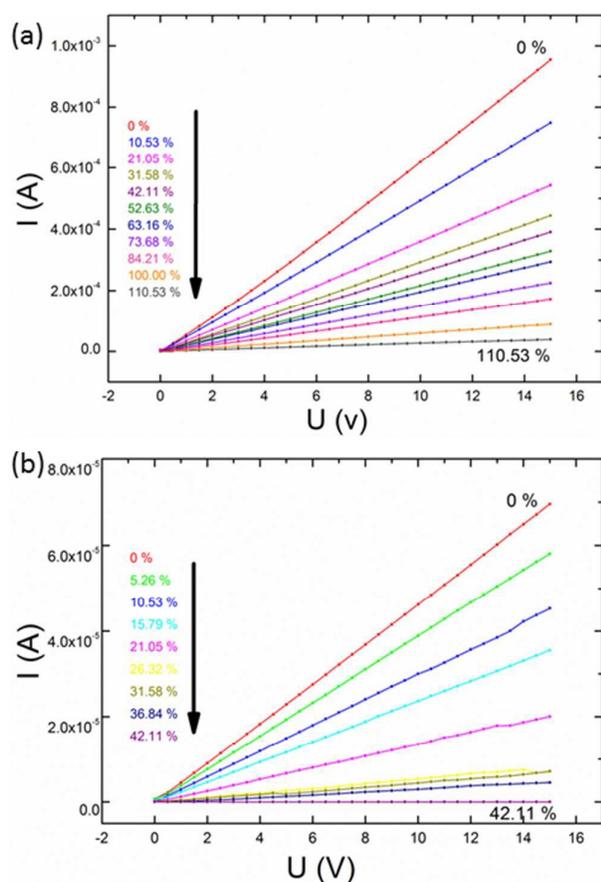


Fig. 4. I-V curves under different strains. (a) I-V curves of the patterned sensor under different strains. (b) For comparison, I-V curves of the common nonwoven mat sensor under different strains.

Stretchable electronics have aroused attentions for the potential applications including, but not limited to, deformable light-emitting display,²⁴⁻²⁵ foldable, rollable, and bendable displays,²⁶⁻²⁷ monitor the state of the critical infrastructures made by natural disasters, such as hurricanes and earthquakes,²⁸⁻²⁹ microfluidic devices,³⁰ joint of a sensitive robot,³¹⁻³² personal health monitoring^{30,32-37} and skin like sensors.³⁸ Many efforts have been dedicated to the future electronics to integrate the attributes of lightweight, small, flexibility and stretchability compared to the conventional electronic devices.³⁹ However, pure PANI has poor mechanical properties compared to nonconductive polymers. For example, the stretched pure PANI has poor elasticity,⁴⁰ but it has good personalities of high conductivity, good biocompatibility, and physical robustness.^{41,42} PVDF, has poor conductivity, however, it has good pyroelectric/piezoelectric features, mechanical properties, and easy processability.⁴³ Moreover, the application of nonwoven membrane is limited by its disordered fiber positioning as mentioned above. Herein, the patterned PANI/PVDF membrane has the properties of elasticity, high stretchability and conductivity owing to the fabrication method and the constituents. In the present case, all the stretchabilities of the patterned membranes (Fig. 2) obtained are higher than the unwoven one for the stretchability tests of nearly 100 samples. Here we only take the patterned membrane collected by metal grid (Fig. 3a) as an example. Accordingly, two PANI/PVDF sensors are fabricated in order to show the different strain characteristics. Patterned sensor (1.05 cm × 0.62 cm × 0.03 cm) is made of the patterned PANI/PVDF membrane and the strain direction is the forward direction of the chess board like pattern (Fig. 3a). For comparison, nonwoven mat sensor (1.05 cm × 0.62 cm × 0.03 cm) is fabricated by the common nanofibrous PANI/PVDF membrane. Fig. 4a shows the I-V characteristics of the patterned PANI/PVDF sensor with different uniaxial strains. It can be seen that the sensor can tolerate a strain up to 110.53% at which point the sensor ruptures, moreover, the current decreases gradually with the stretching varying from 0% to 110.53%. For comparison, the maximum strain of the nonwoven mat sensor is much lower than the above patterned one, and the value is about 42.11%, as shown in Fig. 4b. All of these indicate that the patterned membrane sensor has better mechanical characteristic compared to common nonwoven one, indicating its potential application in measuring human motion, tension and strain.³⁹ In addition, one of the most formidable challenges of the stretchable electronics is that it can retain high conductivity even under severe deformation, such as stretching, bending, twisting and folding.³¹ In the present case, the patterned sensor can remain high conductivity even facing the limit of the strain, which also means the potential application of the device as strain sensors.²⁶

The fabricated patterned strain sensor showing a larger strain than the nonwoven one can be mainly ascribed to the configuration of nanofibrous membrane, which is strongly affected by the collector configuration and electric field distribution. Fig. 5 shows the electric field simulations for the cases of using an Al foil and a metal grid as the collector in the electrospinning, which were made using COMSOL Multiphysics V4.2. It can be seen that the electrical field lines have a uniform distribution near the Al foil (Fig. 5a), indicating that the electric field force for charged fibers is uniform over the collector, and thus the electrospun fibers are deposited

randomly and formed a nonwoven membrane. However, for metal grid, a patterned electroconductive collector, the electric field lines are converged toward the metal grid (Fig. 5b), indicating that the charged jet could be moved away from its original deposition track towards the surface of the metal grids owing to the concentrated electric field, and thus a patterned fibrous membrane could be obtained (Figs. 2d and 3b). This patterned configuration is in favor of improving the membrane stretchability. In the process of stretching, the patterned fibrous membrane will undergo two stages: The first one is a large elastic and plastic deformation that makes the curled patterned fibers become nearly straight and parallel; The second one is further plastic deformation and gradual fracture of the fibers. Compared to the common nonwoven membrane, it is obvious that the patterned structure of the fibrous membrane can increase the elastic deformation and thus enhance membrane stretchability.

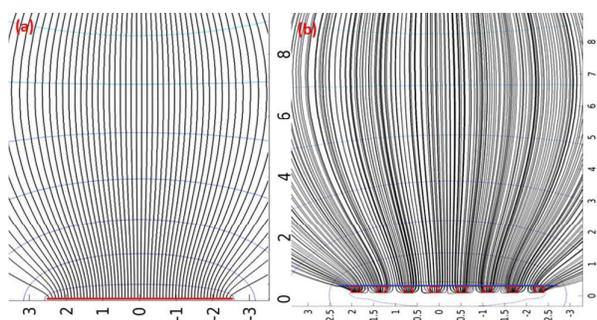


Fig. 5. Electric field simulations for the cases of using an Al foil (a) and a metal grid (b) as the collector in electrospinning.

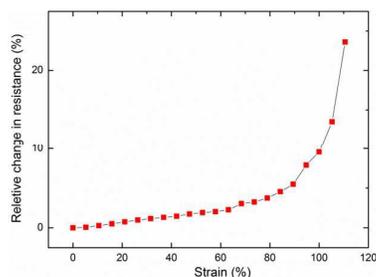


Fig. 6. Relative change in resistance of the patterned sensor under different strains.

As we know, the performance of a strain sensor is characterized by a gauge factor for practical application, which is defined as $(dR/R)/(dL/L)$, meaning the sensitivity of the sensor to strain, here R is the resistance of the sensor, L is the original length.^{39,33,35,36} The relative change in resistance of sensor is characterized by two regions with different slopes and the relative changes in resistance increased steadily, as shown in Fig. 6. The gauge factor is 0.045 (0% to about 85%) and 0.840 (85% to 110.53%) respectively. For comparison, previously reported sensors based on electrospun

PEDOT:PSS/PVA nanofibers¹⁹ or PEDOT:PSS/PVA film⁴⁴ have a very low stretchability but a higher gauge factor. In addition, as a stretchable electronic device, it should have the capacity to absorb a large level of strain without obvious changes in their electrical performance.⁴⁵ Therefore, the results show both good stability of conductivity during the deformation^{32,38} and potential application as strain sensors.³³

3.2 Stability and durability test

A good stretchable electronic device should retain conductivity without significant degradation under various elastic deformations.³² For the purpose of detecting the stability characteristic, the currents under different strains are measured with a fixed voltage of 5.0 V. The sensor is stretched from 0% to 11.2%, and from 11.2% to 22.4%, and 22.4% to 0% step by step, as shown in Fig. 7a. It is showed that the response time and recovery time are only several seconds, furthermore, the current remains the same value under the 0% strain. In a word, the sensor can preserve its original electrical value even under the strain of 22.4%.⁴⁶

Additionally, long time durability is essential for practical applications of the sensor.³⁵ In order to further understand the stability of the device, we investigate the endurance and stability of the PANI/PVDF membrane under cyclic folding and unfolding tests, and the result is shown in Fig. 7b. Curve A is the I-V characteristic of

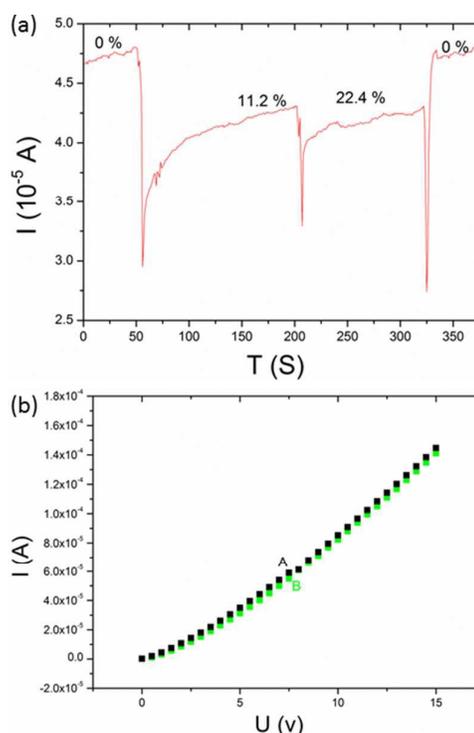


Fig. 7. Stability and endurance tests of the patterned sensor. (a) Current responses of the sensor to different strains under a fixed bias of 5 V; (b) Curve A is the I-V characteristics of sensor at initial state. Curve B is the I-V characteristics of the sensor which is folded for 10,000 folds and kept for 24 h.

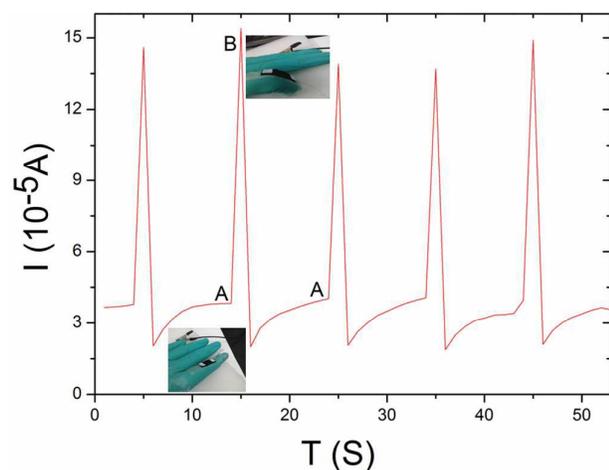


Fig. 8 Current response and photographs of a wearable sensor attached onto a forefinger for monitoring human-motion. (A) A relaxing state of the patterned sensor at the point when the demonstrator's finger is bended suddenly; (B) The maximum response current of the patterned sensor to the finger bending, at the same time the finger is completely unfolded suddenly.

sensor at initial state. Curve B is the state which the sensor is folded for 10,000 folds and stays for 24 h afterwards. It can be seen that conductivity only has a very slight change between the initial state and the 10,000 folding state, demonstrating high repeatability, durability and stability of the device.

3.3 Finger motion detection

Considering that the conventional hospital-centered healthcare sensing devices is limited for the poor portability and wearability,²⁸ the sensor is becoming the frontier for the potential applications in portable and wearable electronics. Many groups have dedicated themselves to incorporating it into smart clothes or attaching it directly to the body to monitor human motions, disease diagnosis, virtual reality and health assessment,^{30,32-38,47} which require for the characteristic of cheap, lightweight, mechanically compliant, and display reasonable sensitivity.³⁴ Considering the fact that fingers undertake the most sophisticated human actions, here, the sensor is assembled on a rubber glove to the forefinger to record the current responses during the bending and unbending actions.³⁸ The current through the sensor of cyclical movements of the fingers at the fixed voltage of 5 V and the cycle is repeated after 10,000 times folding, however, only five ones are shown in Fig. 8. In the process, the finger bends to the nearly the same angle (for the movement of the finger manually, the angle may differ a little) and releases rapidly. When the demonstrator's finger is suddenly bended, as shown in point A, the current increases sharply, meaning the current responds to the actions of the finger is almost immediately. For the angle of the bending finger is not absolutely unanimous, the current may differ a little at the bend point of the finger in every cycle. Furthermore, once the finger is completely unfolded suddenly, the current returns to the initial value sharply. The current can fully recover to its original value at the point of the

unfolding in every cycle. The results indicate that the sensor is capable of monitoring different

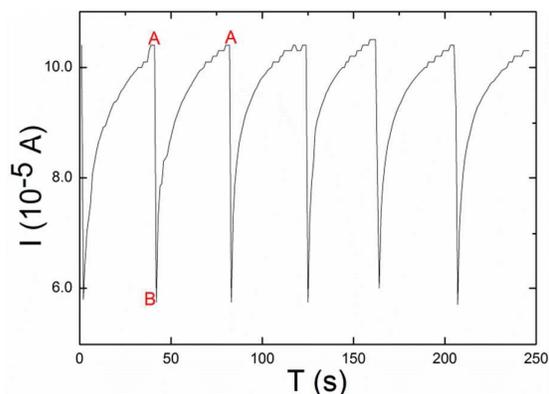


Fig. 9 Current response of the patterned sensor to cyclic tapping. (A) Transition point from a relaxed state to a pressure state when a tapping is imparted suddenly; (B) The maximum response current value is generated by the tapping at this point, and then a relaxed state is given to the patterned sensor with removing the initial pressure.

parts of the human motions, acting as parts of robot, and using as human machine interfacing applications.^{30,32-38,48}

3.4 Pressure-resolved response

To obtain more details of the sensor response, current generation is assessed by tapping the sensor vertically using a quartz lump (5.00 g) with a contact area of 2.25 cm², and the device is also packaged by the PDMS. Fig. 9 shows the typical current output versus time curve of the sensor, which has been tested repeatedly for nearly 10,000 times of folding and only six cycles are listed. The external mechanical tapping has a significant effect on the electric transport of the sensor. When subjected to an external force, the whole device can act like a variable resistor. In Fig. 9, point A means a transition from a relax state to a pressure state of the sensor under a tapping, and point B means the current reaches the maximum response to the tapping, and then a relaxed state is given to the patterned sensor with removing the initial pressure. It can be seen that the sensor has a fast response and the current recovers to the initial value fully after withdrawing the tapping. Under mechanical tapping once more, the device repeats almost the same value of the last circle. Additionally, the sensitivity of the tapping can also be obtained by $S = (\Delta I / I_0) / p$,^{28,35} here p is the applied pressure made by the tapping, ΔI is the current change when tapping is applied on the device, and I_0 is the current without tapping. Result shows that the S is 1.8 kPa⁻¹. This value is comparable to that (1.8 kPa⁻¹) for silk-molded micro-patterned polydimethylsiloxane (PDMS) with a single-walled carbon nanotube (SWCNT) ultrathin film,²⁸ lower than 10.3 kPa⁻¹ of PEDOT:PSS and an aqueous polyurethane dispersion elastomer blend when stretched by 40%,⁴⁹ and higher than 0.33 kPa⁻¹ of polypyrrole/silver coaxial nanowire aero-sponges.⁵⁰ In other words, the sensor has good sensitivity for deformation. The rapid and repeated response of the

sensor demonstrates that it may be directly attached to the clothing for the application of recreation, virtual reality, health care, and even future multi-functional intelligent room.^{26,39,37,47,48}

4. Conclusion

In summary, we report a simple and cost-effective method to fabricate highly stretchable patterned nanofibrous PANI/PVDF strain sensors. The patterned sensor can measure and withstand a strain up to 110%, which is much higher than the common nonwoven one and previously reported values. Moreover, folding and unfolding tests also show some positive qualities, such as stability and durability. The patterned PANI/PVDF sensor is also used to detect pressure and finger motion, which shows fast, stable and repeatable response. These interesting features indicate that the patterned nanofibrous membranes may be used in flexible and stretchable electronic devices.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51373082 and 41476059), the Taishan Scholars Program of Shandong Province, China (ts20120528), the National Science and Technology Support Program (2012BAB15B02) and the Postdoctoral Scientific Research Foundation of Qingdao.

Notes and references

- H. Liu, X. B. Hu, J. Y. Wang, R. I. Boughton, *Macromolecule*, 2002, **35**, 9414.
- C. Y. Huang, B. Dong, N. Lu, N. J. Yang, L.G. Gao, L. Tian, D. P. Qi, Q. Wu, L. F. Chi, *Small*, 2009, **5**, 583.
- K. Ramanathan, M. A. Bangar, M. H. Yun, W. Chen, A. Mulchandani, N. V. Myung, *Nano Lett.*, 2004, **4**, 1237.
- M. X. Wan, *Adv. Mater.*, 2008, **20**, 2926.
- D. Grafahrend, K. H. Heffels, M. V. Bee, P. Gasteier, M. Mölle, G. Boehm, P. D. Dalton, J. Groll, *Nat. Mater.*, 2011, **10**, 67.
- Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.*, 2003, **15**, 353.
- Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K.-H. Kim, C. M. Lieber, *Science*, 2001, **294**, 1313.
- D. Li, Y. Wang, Y. Xia, *Nano Lett.*, 2003, **3**, 1167.
- D. Zhang, J. Chang, *Nano Lett.*, 2008, **8**, 3283.
- D. C. Surrao, S. D. Waldman, B. G. Amsden, *Acta Biomater.*, 2012, **8**, 3997.
- C. Jia, D. Yu, M. Lamarre, P. L. Leopold, Y. D. Teng, H. Wang, *Adv. Mater.*, 2014, **26**, 8192.
- D. H. Sun, C. Chang, S. Li, L. W. Lin, *Nano letters*, 2006, **4**, 839.
- H. Yang, L. Dong, *Langmuir*, 2010, **26**, 1539.
- T. D. Brown, P. D. Dalton, D. W. Huttmacher, *Adv. Mater.*, 2011, **23**, 5651.
- S. M. Park, D. S. Kim, *Adv. Mater.*, 2015, **27**, 1682.
- Q. Cheng, B. L. P. Lee, K. Komvopoulos, S. Li, *Biomacromolecules*, 2013, **14**, 1349.
- S. Zhao, Q. Zhou, Y. Z. Long, G. H. Sun, Y. Zhang, *Nanoscale*, 2013, **5**, 4993.
- D. Zhang, J. Chang, *Adv. Mater.*, 2007, **19**, 3664.
- N. S. Liu, G. J. Fang, J. W. Wan, H. Zhou, H. Long and X. Z. Zhao, *J. Mater. Chem.*, 2011, **21**, 18962.
- B. Sun, Y. Z. Long, S. L. Liu, Y. Y. Huang, J. Ma, H. D. Zhang, G. Shen, S. Xu, *Nanoscale*, 2013, **5**, 7041.
- C. Merlini, R. dos Santos Almeida, M. A. d'Ávila, W. H. Schreiner, G. M. de Oliveira Barra, *Mater. Sci. Eng. B*, 2014, **179**, 52.
- C. Merlini, G. M. D. O. Barra, S. D. A. D. S. Ramôa, G. Contri, R. D. S. Almeida, M. A. d'Ávila, B. G. Soares, *Frontiers in Materials*, 2015, **2**, 14.
- R. Huang, Y. Z. Long, C. C. Tang, H. D. Zhang, *Adv. Mater. Res.*, 2014, **853**, 79.
- J. A. Rogers, T. Someya, Y. G. Huang, *Science*, 2010, **327**, 1603.
- T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, *Nat. Mater.*, 2009, **8**, 494.
- Y. Cheng, R. Wang, J. Sun, L. Gao, *ACS Nano*, 2015, **9**, 3887.
- M. J. Han, D. Y. Khang, *Adv. Mater.*, 2015, **27**, 4969.
- X. W. Wang, Y. Gu, Z. P. Xiong, Z. Cui, T. Zhang, *Adv. Mater.*, 2014, **26**, 1336.
- H. Gullapalli, V. S. M. Vemuru, A. Kumar, A. Botello-Mendez, R. Vajtai, M. Terrones, S. Nagarajaiah, P. M. Ajayan, *Small*, 2010, **6**, 1641.
- H. Ko, J. Lee, Y. Kim, B. Lee, C. H. Jung, J. H. Choi, O. S. Kwon, K. Shin, *Adv. Mater.*, 2014, **26**, 2335.
- T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida, T. Someya, *Science*, 2008, **321**, 1468.
- U. H. Shin, D. W. Jeong, S. M. Park, S. H. Kim, H. W. Lee, J. M. Kim, *Carbon*, 2014, **80**, 396-404.
- Z. F. Liu, S. Fang, F. A. Moura, J. N. Ding, N. Jiang, J. Di, M. Zhang, X. Lepró, D. S. Galvão, C. S. Haines, N. Y. Yuan, S. G. Yin, D. W. Lee, R. Wang, H. Y. Wang, W. Lv, C. Dong, R. C. Zhang, M. J. Chen, Q. Yin, Y. T. Chong, R. Zhang, X. Wang, M. D. Lima, R. Ovalle-Robles, D. Qian, H. Lu, R. H. Baughman, *Science*, 2015, **24**, 400.
- C. S. Boland, U. Khan, C. Backes, A. O'Neill, J. McCauley, S. Duane, R. Shanker, Y. Liu, I. Jurewicz, A. B. Dalton, J. N. Coleman, *ACS Nano*, 2014, **8**, 8819.
- S. Gong, W. Schwalb, Y. Wang, Y. Chen, Y. Tang, J. Si, B. Shirinzadeh, W. Cheng, *Nat. Commun.* 2014, **5**, 3132.
- E. Roh, B. U. Hwang, D. Kim, B. Y. Kim, N. E. Lee, *ACS Nano.*, 2015, **9**, 6252.
- G. S. Jeong, D. H. Baek, H. C. Jung, J. H. Song, J. H. Moon, S. W. Hong, I. Y. Kim, S. H. Lee, *Nat. Commun.*, 2012, **3**, 977.
- X. Q. Liao, Q. L. Liao, X. Q. Yan, Q. J. Liang, H. N. Si, M. H. Li, H. L. Wu, S. Y. Cao, Y. Zhang, *Adv. Funct. Mater.*, 2015, **25**, 2395.
- T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, K. Hata, *Nat. Nanotechnol.*, 2011, **6**, 296.
- T. S. Hansen, K. West, O. Hassager, N. B. Larsen, *Adv. Funct. Mater.*, 2007, **17**, 3069.
- G. A. Gelves, M. H. Al-Saleh, U. Sundararaj, *J. Mater. Chem.*, 2011, **21**, 829.
- S. Bhadra, D. Khastgir, N. K. Singha, J. H. Lee, *Prog. Polym. Sci.*, 2009, **34**, 783.

- 43 W. Huang, K. Edenzon, L. Fernandez, S. Razmpour, J. Woodburn, P. Cebe, *J. Appl. Polym. Sci.*, 2010, **115**, 3238.
- 44 N. Trifigny, F. M. Kelly, C. Cochrane, F. Boussu, V. Koncar, D. Soulat, *Sensors*, 2013, **13**, 10749.
- 45 T. Cheng, Y. Zhang, W. Y. Lai, W. Huang, *Adv. Mater.*, 2015, **27**, 3349.
- 46 X. Xiao, L. Y. Yuan, J. W. Zhong, T. P. Ding, Y. Liu, Z. X. Cai, Y. Z. Cai, Y. G. Rong, H. W. Han, J. Zhou, Z. L. Wang, *Adv. Mater.*, 2011, **23**, 5440.
- 47 M. Shin, J. H. Song, G. H. Lim, B. Lim, J. J. Park, U. Jeong, *Adv. Mater.*, 2014, **26**, 3706.
- 48 T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida, T. Someya, *Science*, 2008, **32**, 1468.
- 49 C. L. Choong, M. B. Shim, B. S. Lee, S. Jeon, D. S. Ko, T. H. Kang, J. Bae, S. H. Lee, K. E. Byun, J. Im, Y. J. Jeong, C. E. Park, J.-J. Park, U. I. Chung, *Adv. Mater.*, 2014, **26**, 3451.
- 50 W. He, G. Li, S. Zhang, Y. Wei, J. Wang, Q. Li, X. Zhang, *ACS Nano*, 2015, **9**, 4244.