Photo-Patternable, High-Speed Electrospun Ultrafine Fibers Fabricated by Intrinsically Negative Photosensitive Polyimide

Lin Qi, Yan-jiang Jia, Yuan-cheng An, Xin-xin Zhi, Yan Zhang, Jin-gang Liu,* and Jia-shen Li*

1. INTRODUCTION

Wearable devices present great value and potential in domains of movement data collection, multidevice collaboration, and human health management.1 However, most of the current ones are composed of hard plastic shells and dense polymer films.2 On the one hand, they cannot fit the human skin completely, which may lead to imprecise data collection of the daily physical body movements. On the other hand, the lower air permeability of such materials may cause physiological discomfort and even anaphylaxis, which also limits the actual applications of such electronics.3 Fibers, as one of the oldest and most familiar materials of mankind, have now begun to emerge in the field of electronic materials. Fiber-based electronic devices with one-dimensional architecture have attracted great interest in wearable electronic domain.4,5 Compared with traditional flexible devices, fibrous electronics are flexible and lightweight and can adapt to different shape deformations such as bending, distortion, and stretching. Meanwhile, the fibrous structure endows enough breathability to reduce discomfort for the human body. Hence, a lot of researchers have put their efforts into combining fibers and textiles with microelectronics, aiming at achieving high-sensitive and biocompatible wearable electronic devices.6–8 Although fibrous devices with multilayer membrane structures have been constructed, current existing research studies can merely achieve basic sensing capabilities.9,10 This is undoubtedly inadequate for the practical application of such devices. To further expand the functionality of fiber-based wearable devices, it is necessary to endow fibers to form hierarchical structures with different patterns at the micro- or nanolevel by photolithographic methods to achieve improved sensing capabilities and multiple functions.11–13 Thus, it is necessary to prepare fiber-based products that can produce differences in solubility under ultraviolet (UV) light irradiation, thereby obtaining micropatterns with different shapes. So far, a variety of methods have been used to prepare fibers with photo-cross-linking properties, such as inducing photoactive pyrimidine,14 photo-cross-linkable cinnamate function groups,15 acrylic moieties with unsaturated C=C bonds,16,17 and making use of thiol–ene photopolymerization.18–20

At present, the combination of UV-induced cross-linking and ultrafine fibers is proposed, but the hinge lies in the practical application of such fibers to lithography. Research on fiber-based lithography has been ongoing since 2010.21 Various photosensitive polymeric fibers have been applied to form arrayed structures for flexible circuits and even biomedical applications.22–24 However, two main defects limit further applications of such materials. First, the poor thermostability of traditional polymer fibers may lead to the dimension loss of the micropatterns during the baking procedure, which is undoubtedly disadvantageous to lithography. Second, normal flexible electronics fabricated by randomly arranged fibers tend to present lower mechanical strength and durability and hence find it difficult to withstand times of deformation and bending.

Received: May 14, 2021
Accepted: June 18, 2021
Published: July 2, 2021
resulting in adverse effects on the reliability of the whole device.

To solve the above problems, we have made the following attempts. First, the organo-soluble intrinsically negative photosensitive polyimide (PSPI) was utilized as a fiber-forming agent, aiming at obtaining fibers with both superior thermal resistance and lithography eligibility. A short time UV irradiation is sufficient to activate the benzophenone moiety in the main chain to generate hydrogen extraction reactions, resulting in free radical cross-linking. Besides, the self-cross-link nature of the PSPI avoids the pyrolysis of small molecular additives during the heating process, which greatly improves the shape retention ability during lithography. Second, the high-speed electrospinning procedure was applied to improve the mechanical properties of the prepared fiber membrane. Through increasing the rotating speed of the collector, an outer force along the circumference is applied to the electrospun fibers to stretch the nascent fiber in a fixed direction, thereby fabricating fibers with aligned structure. Such fibers exhibit aligned arrangement along one direction, smooth and straight fibrous morphology, and enhanced mechanical property with the increase of the collection speed. The ultrafine fibrous membranes (UFMs) represent good deformation and folding ability, favorable hydrophobicity, and optical property, which are appropriate for applications on flexible electronics. In addition, the UFM can achieve micron-level patterns through a simple lithography process and can retain its fibrous structure.

2. MATERIALS AND METHODS

2.1. Materials. The intrinsically negative PSPI was synthesized according to our previous literature. The organic solvents N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF) were both supplied by Sigma-Aldrich Co. Ltd, China, and distilled prior to use. The electrospinning device was purchased from Yongkang-Leye (Beijing, China), and a high-speed collector with a maximum rotating speed of 3000 rpm was used for the accumulation of the fibers.

2.2. Preparation of PI Ultrafine Fibrous Membranes. 1.5 g of synthesized PI resin was dissolved into 8.5 g of DMAc to form a 15% wt PI solution with the viscosity of 1800 mPa·s. Then, a typical electrospinning procedure was performed with an applied voltage of 15 kV, flow rate of 10 μL/s, and collector-spinneret distance of 10 cm. The temperature and humidity were fixed at 26 °C and 30 ± 5%, respectively. The fibers were obtained on a layer of aluminum foil covered on the collector. A high-speed rotating collector was used to obtain aligned ultrafine fibers, whose speed was 1000, 1500, 2000, and 2500 rpm.

2.3. Measurements. The morphology of the fibers was observed by scanning electron microscopy (SEM, JEOL-JIT300, Tokyo, Japan), with the accelerating voltage of 20 kV and a 20 nm layer of Pt/Pd deposited prior to observation. The software ImageJ was used for measurement and statistical analysis of the fiber diameters, with the values counted from 100 single fibers. A Dataphysics OCA 40 contact angle instrument (Stuttgart, Germany) was utilized to measure the water contact angle (WCA) of the UFMs, whose specific value was determined from the averages of five measurements.
mechanical property of the UFMs was investigated by a Shimazu AGS-X 1kN (Kyoto, Japan) electromechanical universal testing machine at a tensile speed of 5 mm/min. The UFM samples were cut into thin strips with 3 mm width, 10 mm length, and 0.15 mm thickness. For the optical property, a Hitachi U-3210 spectrophotometer (Tokyo, Japan) was utilized to measure the ultraviolet–visible (UV–vis) reflectance spectrum at room temperature, and an X-rite Ci 7800 spectrophotometer (Michigan, USA) was used to measure the yellowness index (YI) of the UFMs according to the ISO 11475: 2017 standard (CIE whiteness, D65/10°, outdoor daylight).

The patterning ability was investigated by a simplified photolithography procedure. Briefly, the UFM was closely covered with a 4-inch mask and exposed to a Hamamatsu GL-250 (Hamamatsu, Japan) ultraviolet light source for 30 s, whose wavelength was fixed at 365 nm (i-line) and the radiant energy fixed at 4 W/cm². After exposure, the UFM was rapidly developed in DMF for 3 s and then dried at 180 °C for 30 min in a vacuum baking oven. The micropatterns of the PI UFM were confirmed by SEM measurement.

3. RESULTS AND DISCUSSION

High-speed electrospinning is a versatile method for obtaining PI UFM with enhanced strength and toughness. The fabricated UFMs possess favorable bending resistance and flexibility, and they can be folded into multilayers and different shapes and reinstated with no breakages and other structural damages (Figure 1b). The SEM images manifest that uniformly aligned fibers were obtained, and no morphological defects like beads or spindle-shaped defects were observed. The alignment degree increases with the rotation speed of the collector. All fibers retain low diameters within one micron and exhibit homogeneous diameter distribution, whose average value increases from 304 nm to 599 nm with the rotating speed (Table 1). Such a good fibrous morphology indicates the rationality of the settled electrospinning parameters, leading to proper balance among the electrostatic repulsion force of the spray microjets, the viscoelastic force of the PI solution, and the tensile force of the rotating collector. In addition, the differences in average diameters are mainly ascribed to enhanced mass transfer between the nascent fiber and the external environment from the motived air motion during the high-speed collector, resulting in faster evaporation and impeding further stretching of the charged spray jets.

Figure 2 illustrates the wettability and mechanical property of the aligned PI UFMs. Owing to the synergistic effect of the low surface energy of the rough fibrous structure and the induced hydrophobic trifluoromethyl moieties, the WCA of PI UFMs expresses all higher than 90°, manifesting as hydrophobicity (Figure 2a,b). In addition, the WCA decreases from over 130° to 126.3° as the fiber diameter increases, suggesting that thinner fibers lead to better hydrophobicity and indicating that high roughness structure benefits to form a surface with self-cleaning property, which is a crucial aspect for the long-term use of fiber-based wearable devices. The mechanical performance of the UFMs is shown in Figure 2c,d. A 5 mm width, 100 mm length aligned PI UFM strip can bear the load of 1 kg, which is thousands of times heavier than itself, indicating that high-speed electrospinning can easily improve the toughness of the microfibers by providing an aligned structure. The high-speed electrospinning makes the fibers plastically stretched during fabrication. Such stretching drives the PI molecular chains to arrange along the direction of the force so that the covalent bond acts as the dominant force between the atoms in the alignment direction, rather than the van der Waals force. This greatly enhances the mechanical strength of the fibers along the aligned direction. To be specific, the tensile strength is in direct proportion to the collection speed, which enhances from 3.99 MPa (PI-1000) to the maximum value of 9.18 MPa (PI-2500). Such favorable mechanical strength and hydrophobicity lead to better durability, which is indispensable for the actual applications of the PI UFMs.

Figure 3 illustrates the influence of the rotating speed on the optical property of the UFMs. Profited from the fibrous structure, the tested samples express light color, similar to the background paper. The reflectance increases to over 80% from 300–400 nm wavelength and finally reaches up to the maximum at 800 nm. All aligned PI UFMs exhibit high blue-gray whiteness (the reflectance at 457 nm wavelength), higher than 84%. Changes in the rotating speed make no significant difference to the UV–vis spectrum of the UFMs. YI measurement further demonstrates that the lightness (L) gradually decreases from 95.5 to 94.5 with the increment of the rotating speed. This is ascribed to the highly aligned fibers that allow the reflected light to propagate along a fixed direction to a certain extent, leading to enhanced reflection orderliness, which hinders diffuse reflection and thus leads to higher YI (Table 1).

The PI-2500 UFM was applied to the photo-patterning procedure. The unexposed area dissolved immediately because of the organo-soluble nature of the utilized PI resin. Conversely, the exposed area still remained after the developing procedure by DMF, according to the Supporting Movie. As shown in Figure 4a, after development by DMF and the postbaking procedure, clearly alphabetic patterns were retained on the surface of the aluminum substrate. The obtained patterns ascribe to the hydrogen abstraction of the UV-activated triplet ketone carbonyl moieties in the PI main chains, initiating the subsequent free radical cross-linking (Figure 4b), which decreases the free volume of PI and hinders the invasion of the solvent DMF. As shown in Figure 5a, despite the generated chemical bonds that exactly enhanced the interactions of the molecular chains, the XRD measurements indicate that the UV exposure made no apparent differences in the crystallinity of the PI UFM, which expresses as the amorphous state. The lithography of the PI UFM acquired patterns with a maximum width of 132.4 μm and a minimum width of 67.3 μm. The EDX spectrum demonstrates that most of the element carbon from the PI molecular chains are located on the obtained patterns, while the outer part is mainly composed of aluminum of the substrate. A higher
magnification image indicates that owing to the strong solvent effect of DMF, fibers swelled and dissolved partly, leading to the loss of the original morphology. However, the fibrous structure still reserved, indicating that the cross-linking reactions can exist even in a solid fibrous structure where the molecular chain movements are relatively restricted. The superior photosensitivity of the PI fibers permits the formation of fiber-based micropatterns directly by normal lithography.
procedure. The critical dimension was obtained at 82.4 μm, achieved by the 96 μm-width grating, accounting for pattern retention degree at 85.83%, and manifesting favorable patterning ability.

4. CONCLUSIONS

This study successfully fabricated PI UFMs with aligned structures by the high-speed electrospinning procedure. The UFMs exhibit enhanced mechanical strength with tensile strength higher than 9 MPa, good elasticity with elongation at break of 24.56%, favorable hydrophobicity with WCA over 126°, and optical property with YI lower than 17%. In addition, the photosensitivity of the PI UFMs allows for achieving fibrous microstructures directly on soft substrates by photolithographic methods at relatively high accuracy. These phenomena are undoubtedly of great significance for the realization of all-fiber flexible electronic devices with complex multilevel structures and functions in the future.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02535.

Developing procedure of the PI UFM (MP4)

**AUTHOR INFORMATION**

Corresponding Authors

Jin-gang Liu — Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China; orcid.org/0000-0001-6629-1646; Email: liujg@cugb.edu.cn

Jia-shen Li — Lecturer of Nano-functional Fibres, School of Materials, The University of Manchester, Manchester M13 9PL, U.K.; orcid.org/0000-0001-7333-5280; Email: jia.shen.li@manchester.ac.uk

**Figure 4.** (a) Lithography procedure of the PI UFMs; (b) photo-cross-linking mechanism of the PI fibers; (c) micropatterns obtained by the PI UFMs.

**Figure 5.** (a) XRD spectrum of the exposed and unexposed PI UFMs, micropatterns (b) and the remained fibrous structure (c) obtained from the PI UFMs, micropatterns obtained from a 96 μm width grating (d), and the corresponding EDX spectrum of the C (e) and Al (f) elements.
Authors
Lin Qi — Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials Science and Technology, China University of Geosciences, Beijing 100083, China
Yan-jiang Jia — Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
Yuan-cheng An — Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
Xin-xin Zhi — Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
Yan Zhang — Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02535

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial supports from the Shandong Key Research and Development Program (no. 2019JZZY020235) and the Fundamental Research Funds of China University of Geosciences, Beijing (no. 2652017345) are gratefully acknowledged.

REFERENCES

(1) Wang, L.; Fu, X.; He, J.; Shi, X.; Chen, T.; Chen, P.; Wang, B.; Peng, H. Application Challenges in Fiber and Textile Electronics. Adv. Mater. 2020, 32, 1901971.
(2) Chen, G.; Li, Y.; Bick, M.; Chen, J. Smart Textiles for Electricity Generation. Chem. Rev. 2020, 120, 3668–3720.
(3) Cherenack, K.; Zysset, C.; Kinkeldei, T.; Münzenrieder, N.; Tröster, G. Woven Electronic Fibers with Sensing and Display Functions for Smart Textiles. Adv. Mater. 2010, 22, 5178–5182.
(4) Zeng, W.; Shu, L.; Li, Q.; Chen, S.; Wang, F.; Tao, X. Fiber-Based Wearable Electronics: A Review of Materials, Fabrication, Devices, and Applications. Adv. Mater. 2014, 26, 5310–5336.
(5) Wang, C.; Xia, K.; Wang, H.; Liang, X.; Yin, Z.; Zhang, Y. Advanced Carbon for Flexible and Wearable Electronics. Adv. Mater. 2018, 31, 1801072.
(6) Liu, N.; Liu, Y.; Zhao, Y.; Liu, Y.; Lan, Q.; Qiu, J.; Song, Z.; Zhan, H. CNT-Intertwined Polymer Electrode toward the Practical Application of Wearable Devices. ACS Appl. Mater. Interfaces 2019, 11, 46726–46734.
(7) Wang, Q.; Jian, M.; Wang, C.; Zhang, Y. Carbonized Silk Nanofiber Membrane for Transparent and Sensitive Electronic Skin. Adv. Funct. Mater. 2017, 27, 1605657.
(8) Bi, P.; Liu, X.; Yang, Y.; Wang, Z.; Shi, J.; Liu, G.; Kong, F.; Zhu, B.; Xiong, R. Silver-Nanoparticle-Modified Polyimide for Multiple Artificial Skin-Sensing Applications. Adv. Mater. Technol. 2019, 4, 1900426.
(9) Zhao, J.; Wu, G.; Hu, Y.; Liu, Y.; Tao, X.; Chen, W. A Wearable and Highly Sensitive CO Sensor with Macroscopic Polyimine Nanofiber Membrane. J. Mater. Chem. A 2015, 3, 24333–24337.
(10) Li, B.; Zhang, F.; Guan, S.; Zheng, J.; Xu, C. Wearable piezoelectric device assembled by one-step continuous electrospinning. J. Mater. Chem. C 2016, 4, 6988–6995.
(11) Kim, W.; Kwon, S.; Han, Y. C.; Kim, E.; Choi, K. C.; Kang, S.-H.; Park, B.-C. Reliable Actual Fabric-Based Organic Light-Emitting Diodes: Toward a Wearable Display. Adv. Electron. Mater. 2016, 2, 1600220.
(12) Zhang, L.; He, J.; Liao, Y.; Zeng, X.; Qiu, N.; Liang, Y.; Xiao, P.; Chen, T. A self-protective, reproducible textile sensor with high performance towards human–machine interactions. J. Mater. Chem. A 2019, 7, 26631–26640.
(13) Rein, M.; Favrod, V. D.; Hou, C.; Khudiyev, T.; Stolyarov, A.; Cox, J.; Chung, C.-C.; Chhav, C.; Ellis, M.; Ioannopoulos, J.; Fink, Y. Diode fibres for fabric-based optical communications. Nature 2018, 560, 214–218.
(14) Wang, Y.-S.; Cheng, C.-C.; Ye, Y.-S.; Yen, Y.-C.; Chang, F.-C. Bioinspired Photo-Cross-Linked Nanofibers from Uracl-Functionalized Polymers. ACS Macro Lett. 2012, 1, 159–162.
(15) Gupta, P.; Trenor, S.; R.; Long, T.; E.; Willks, G. L. In Situ Photo-Cross-Linking of Cinnamate Functionalized Poly(methyl methacrylate-co-2-hydroxyethyl acrylate) Fibers during Electrospinning. Macromolecules 2004, 37, 9211–9218.
(16) Kim, S. H.; Kim, S.-H.; Nair, S.; Moore, E. Reactive Electrospinning of Cross-Linked Poly(2-hydroxyethyl methacrylate) Nanofibers and Elastic Properties of Individual Hydrogel Nanofibers in Aqueous Solutions. Macromolecules 2005, 38, 3719–3723.
(17) Zhang, H.; Niu, Q.; Wang, N.; Nie, J.; Ma, G. Thermo-sensitive drug controlled release PLA core/PNIPAM shell fibers fabricated using a combination of electrospinning and UV photo-polymerization. Eur. Polym. J. 2015, 71, 440–450.
(18) Shanmuganathan, K.; Elliot, S. M.; Lane, A. P.; Ellison, C. J. Highly Stretchable Thermoset Fibers and Nonwovens Using Thiol–Ene Photopolymerization. ACS Appl. Mater. Interfaces 2014, 6, 14259–14265.
(19) Niu, Q.; Zeng, L.; Mu, X.; Nie, J.; Ma, G. Preparation and characterization of core-shell nanofibers by electrospinning combined with in situ UV photopolymerization. J. Ind. Eng. Chem. 2016, 34, 337–343.
(20) Thiellke, M. W.; Bruckner, E. P.; Wong, D. L.; Theato, P. Thiolene modification of electrospun polybutadiene fibers crosslinked by UV irradiation. Polymer 2014, 55, 5996–5999.
(21) Carlberg, B.; Wang, T.; Liu, J. Direct Photolithographic Patterning of Electrospun Films for Defined Nanofibillar Microarchitectures. Langmuir 2010, 26, 2235–2239.
(22) Ji, S.; Hyun, B. G.; Kim, K.; Lee, S. Y.; Kim, S.-H.; Kim, J.-Y.; Song, M. H.; Park, J.-U. Photo-patternable and transparent films using cellulose nanofibers for stretchable origami electronics. NPG Asia Mater. 2016, 8, No.e299.
(23) Kalaoglu-Altan, O. I.; Sanyal, R.; Sanyal, A. Micropatterned Reactive Nanofibers: Facile Fabrication of a Versatile Biofunctionalizable Interface. ACS Appl. Polym. Mater. 2020, 2, 4026–4036.
(24) Hu, H.; Buddingh, J. V.; Wang, Z.; Becher-Nienhaus, B.; Liu, G. Patterning electrospun nanofiber mats for screen printing and other applications. J. Mater. Chem. C 2018, 6, 808–813.
(25) Stoppa, M.; Chiolerio, A. Wearable Electronics and Smart Textiles: A Critical Review. Sensors 2014, 14, 11957–11992.
(26) Fu, M.-C.; Higashihara, T.; Ueda, M. Recent progress in thermally stable and photosensitive polymers. Polym. J. 2017, 50, 57–76.
(27) Vanherck, K.; Koeckelberghs, G.; Vankelecom, I. F. J. Crosslinking polymides for membrane applications: A Review. Prog. Polym. Sci. 2013, 38, 874–896.
(28) Deng, J.; Wang, L.; Liu, L.; Yang, W. Developments and new applications of UV-induced surface graft polymerizations. Prog. Polym. Sci. 2009, 34, 156–193.
(29) Li, L.; Qinghua, L.; Jie, Y.; Zikang, Z.; Daocheng, P.; Zongguang, W. Preparation and properties of photosensitive polyimide/titania–silica hybrid materials. Mater. Sci. Eng., C 2002, 22, 61–65.
(30) Liaw, D.-J.; Wang, K.-L.; Huang, Y.-C.; Lee, K.-R.; Lai, J.-Y.; Ha, C.-S. Advanced polyimide materials: Syntheses, physical properties and applications. Prog. Polym. Sci. 2012, 37, 907–974.
(31) Fukukawa, K.-i.; Ueda, M. Recent Progress of Photosensitive Polyimides. Polym. J. 2008, 40, 281–296.
(32) Xue, J.; Wu, T.; Dai, Y.; Xia, Y. Electrospinning and Electrospun Nanofibers: Methods, Materials, and Applications. Chem. Rev. 2019, 119, 5298–5415.
(33) Xue, J.; Xie, J.; Liu, W.; Xia, Y. Electrospun Nanofibers: New Concepts, Materials, and Applications. Acc. Chem. Res. 2017, 50, 1976–1987.
(34) Ding, Y.; Hou, H.; Zhao, Y.; Zhu, Z.; Fong, H. Electrospun polyimide nanofibers and their applications. Prog. Polym. Sci. 2016, 61, 67–103.
(35) Qi, L.; Liu, J. g.; Yang, Y.; Guo, C. y.; Huangfu, M. g.; Zhang, Y. Solvent-resistant ultrafine nonwoven fibrous membranes by ultraviolet-assisted electrospinning of organo-soluble photosensitive polyimide resin. Polymers 2021, 138, 50048.