

small

Solar Cells

Stretchable Polymer Solar Cell Fibers

*Zhitao Zhang, Zhibin Yang, Jue Deng, Ye Zhang, Guozhen Guan, and Huisheng Peng**

Compared to inorganic photovoltaic devices based on silicon, polymer solar cells (PSCs) show many unique and useful properties such as easy fabrication, low cost and the possibility to be assembled into various flexible products.^[1-7] They have been proposed for the use in a broad spectrum of fields, particularly, electronic skins or integration into clothes that are key to next-generation electronics.^[8] For this, PSCs are required to have other desired properties, such as light weight and weavability, for practical fabric applications. However, these cannot be achieved by the generally studied planar PSCs. Learning from textile technology by using chemical fibers as building units, several groups have recently attempted to develop PSCs in a fiber format.^[9,10] These fibershaped PSCs have also been explored for weaving into thin textiles, however, both fiber-shaped and textile-like PSCs were not found to be stretchable, and are likely to get damaged by the generated stresses during movements that often occur in use. Therefore, for practical applications it is not enough for PSCs to be flexible, they also need to be stretchable.

Here a flexible and stretchable fiber-shaped PSC is developed on the basis of an elastic substrate and a spring-like structure. The fiber-shaped PSC is fabricated by winding an aligned carbon nanotube sheet onto a spring-like electrode that is attached to an elastic fiber as the substrate, whereby a layer of photoactive materials has been coated onto the spring-like electrode. These fiber-shaped PSCs can be further woven into the desired PSC textile. Such PSC fibers and textiles exhibit reasonable energy conversion efficiencies that vary less than 10% after being bent for 1000 times and under stretching at a strain of above 30%.

Figures 1 and S1 (Figure S1 in the Supporting Information) schematically show the fabrication of the stretchable fiber-shaped PSC. A titanium wire was first wound onto a fiber substrate such as steel wire and then removed from the steel wire to produce a spring-like structure. Aligned TiO_2

Z. Zhang, Z. Yang, J. Deng, Y. Zhang, G. Guan, Prof. H. Peng State Key Laboratory of Molecular Engineering of Polymers Department of Macromolecular Science and Laboratory of Advanced Materials Fudan University Shanghai 200438, China E-mail: penghs@fudan.edu.cn. DOI: 10.1002/smll.201400874



nanotubes were then grown in a direction perpendicular to the outer surface of the Ti spring using an electrochemical process. Then, the photoactive materials, poly(3-hexyl thiophene):phenyl-C₆₁-butyric acid methyl ester (labeled as P3HT:PCBM), and the hole-transfer layer consisting of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were sequentially coated onto the modified Ti spring. An elastic fiber, such as rubber, was then inserted into the modified Ti spring. The final step for fabricating a fibershaped PSC was winding a thin layer of continuous carbon nanotube sheet (ca. 18 nm in thickness) onto the resulting Ti



Figure 1. Schematic illustration of the fabrication of a stretchable fibershaped PSC.

communications



Figure 2. Structural characterization of the stretchable fiber-shaped PSC. a) Perpendicularly aligned TiO_2 nanotubes, top view. b) PEDOT:PSS layer on the P3HT:PCBM layer that was coated on the TiO_2 nanotube array, top view. c) SEM image of the spring-like modified Ti wire after coating of the PEDOT:PSS layer. d) SEM image of the spring-like Ti wire inserted with an elastic fiber. e) MWCNT sheet (inset: high magnification). f) Photograph of a fiber-shaped PSC.

spring. The carbon nanotube exhibits a multi-walled structure and is therefore labeled "MWCNT". These MWCNT sheets were produced by pulling from spinnable MWCNT arrays that were synthesized according to the procedure detailed in the Supporting Information (Figure S2).^[11]

Figure 2a exhibits a scanning electron microscopy (SEM) image of the TiO₂ nanotubes attached to the titanium wire (Figure S3, Supporting Information). Here, the TiO₂ nanotube arrays serve as the electron-transfer layer to enhance both separation and transport of produced charges in the fiber-shaped PSC.^[12-15] The diameters ranged from 100 to 150 nm (Figure S4, Supporting Information), whereas the lengths of the TiO₂ nanotubes could be tuned in a range from 650 nm to 4 µm by extending the growth time (in a range of 1–30 min).^[14] The TiO₂ nanotube-modified Ti spring could be attached easily to the two polymer-based layers of P3HT:PCBM and PEDOT:PSS. Figure S5 (Supporting Information) and Figure 2b show SEM images of the two polymerbased layers. Both of them appeared to be uniform without obvious aggregates, which proved necessary to effectively wind the MWCNT-based sheet. Figure 2c further shows the resulting spring-like titanium wire after deposition of the two polymer-based layers with smooth and uniform surfaces. For the P3HT:PCBM layer the thickness was appropriately 80 nm; for the PEDOT:PSS layer, the thickness was measured



to be around 100 nm. Figure 2d shows the effective insertion of a rubber fiber into the modified spring-like titanium wire, whereas Figure 2e verifies the close contact between the MWCNT sheet that has a thickness of about 30 nm and the spring-like titanium wire. The MWCNTs remained highly aligned to each other, which was critically important to the high performance of the fiber-shaped PSC. The titanium electrode as well as the MWCNT sheet served as the electrodes, and the oriented structure of the MWCNTs guaranteed high and stable electrical conductivities under various deformations such as bending and stretching. Figure 2f and Figure S6 (Supporting Information) show the final fiber-shaped PSC. The titanium wire and the MWCNT sheet were connected to an external circuit for the convenience of the following study.

Figure S7a–c in the Supporting Information shows the SEM images of springlike Ti wires with increasing pitch distances from 350 to 490 and 1080 µm, respectively. The pitch distance of the spring-like Ti wire may be accurately tuned by changing the angles between the titanium and steel wire substrates.^[11c] Figure S7d further compares the stress–strain curves between the pure elastic fiber and stretchable PSCs with different pitch distances. It was found that the pitch distance does not obviously affect the mechanical performance of the

PSC. Similar to its role in conventional planar PSCs, the bulk P3HT:PCBM heterojunction layer was designed to perform the solar energy conversion functionality. More specifically, the realization process in the fiber-shaped PSC is demonstrated in Figure S8 (Supporting Information).^[16] After the device was exposed to sunlight, the heterojunction layer produced excitons that were separated to form holes and electrons. The generated holes were collected by the MWCNT layer through the PEDOT:PSS layer, whereas the electrons were transferred to the Ti wire through the aligned TiO₂ nanotube electron-transfer layer. The characterization of energy conversion efficiencies was carried out using standard illumination (100 mW cm⁻²). It was found that the power-conversion efficiency (PCE) improved with the length of the TiO₂ nanotubes from 0.65 to 1.8 µm after which it decreased with further increasing length up to 2.2 µm. Figure S9 in the Supporting Information represents typical J-V curves of fibershaped PSCs at three lengths, namely, 0.65, 1.8, and 2.2 µm. The increasing energy-conversion efficiency with increasing length of TiO₂ nanotubes may be explained by the higher polymer loading at longer TiO₂ nanotubes from 650 nm to 1.8 µm, whereas the following decreasing energy-conversion efficiency can be derived from the longer diffusion pathway for the charges with further increasing length.^[13] Therefore, the optimal length of 1.8 µm was used, unless otherwise specified.



www.MaterialsViews.com

The aligned TiO₂ nanotubes attached to the spring-like Ti wire played a critical role in the high photovoltaic performance. When a bare Ti wire without aligned TiO₂ nanotubes was used under the same conditions, the energy-conversion efficiency was very low.^[11e] It is well known that for most nanoparticles, which often aggregate into various networked structures, the generated charges have to be transported through a lot of boundaries and experience long pathways during diffusion, with poor PCEs as a result. On the contrary, the charges can be more rapidly and effectively transported along aligned TiO₂ nanotubes.^[13] The aligned TiO₂ nanotubes thus enhance the electron transport, which mainly increases the short-circuit current. In addition, as previously mentioned, the spring-like titanium wire coated with TiO₂ nanotubes could also be easily coated with two uniform polymer-based layers. Although these two polymer layers and the MWCNT sheet (Figure S10, Supporting Information) may reduce the overall access of sunlight penetrating into the device, in this work such a phenomenon could be neglected because of the high transmittances of the above layers.^[17] The aligned structure of the MWCNTs enhanced the charge separation and transport.^[18] The MWCNT sheet could be tightly wound on the spring-like modified Ti wire, which can effectively collect the generated holes in the PSC. In addition, the aligned MWCNT sheet that was wound on the outer surface of the fiber-shaped PSC rendered a high stability (Figures S11 and S12, Supporting Information). Because of its one-dimensional structure, the PCE of the fiber-shaped PSC is independent

of the angle of the incident light. The photovoltaic parameters do not obviously vary when the angle of incident light is changed within a range of $0-180^{\circ}$ (Figure S13, Supporting Information), so our fiber-shaped PSC can effectively work under any direction.

Figure 3a shows photographs of the fiber-shaped PSC before and after stretching, and no damage was observed after stretching. Figure 3b further shows the comparison of a one-dimensional PSC before and after stretching (stretched by 30% for 100 times). Before stretching, the PSC showed a PCE of 1.23% with an open-circuit voltage of 0.51 V, short-circuit current density of 6.33 mA cm⁻², and fill factor of 37.9%. The area used for calculating the photovoltaic parameters was estimated on the basis of the effective irradiation from the cathode.^[11c] After stretching, the PCE decreased slightly to 1.19%. Note that although the highest PCE of 1.23% was achieved, these fiber-shaped PSCs still generally exhibited efficiencies around 0.7%.

Figure 3c further compares the incident photon-to-current efficiency (IPCE) curves of the one-dimensional PSC before and after stretching treatment (stretched by 30% for 100 times). It is clear from this figure that the IPCE remains almost unchanged. Figure 3d further shows the energyconversion efficiencies at increasing strains beyond 30%. Although the energy-conversion efficiency had been maintained at 88% for strains up to 40%, the fiber-shaped PSC did not fully return to its original length when the tensile stress was released, in other words, the deformation was



Figure 3. Characterization of the stretchable property of the fiber-shaped PSC. a) Photograph of a fiber-shaped PSC before and after stretching. b) Typical *J*–*V* curve of a fiber-shaped PSC before and after stretching by 30%. c) IPCE curves of a fiber-shaped PSC before and after stretching by 30%. d) Dependence of energy-conversion efficiency on strain of a fiber-shaped PSC. η_0 and η correspond to the energy conversion efficiencies before and after stretching.

communications





Figure 4. a) Photograph of a fiber-shaped PSC with increasing strain from 0 to 80%. b) Dependence of the electrical resistance on the strain for a fiber-shaped PSC. R_0 and R correspond to the resistance before and after stretching, respectively. c,d) SEM images of the PEDOT:PSS layer before and after stretching by 30%, respectively. e,f) SEM images of the aligned MWCNT layer before and after stretching by 30%, respectively.

only partially reversible. Further increasing the strain to 50%, 60%, and 70% resulted in a decrease in the energyconversion efficiency to 50%, 32%, and 21% of the original value, respectively. The fiber-shaped PSCs also retained their stretched shape after relaxation, so again, the deformations were not reversible. At a strain of 80% the fiber-shaped PSC broke.

The mechanism of the stretchable properties of the fibershaped PSC were further studied by SEM (**Figure 4**a and Figure S14, Supporting Information). No obvious damage was observed in the structure after stretching to a strain of 30%. Figure 4c,d shows the PEDOT:PSS layer and Figure 4e,f shows the aligned MWCNT sheet before and after stretching to 30%, respectively. From these figures it is apparent that the polymer layer remains uniform and continuous and the MWCNTs retained their high alignment after stretching. Therefore, the PCEs were maintained at 97%. Stretching beyond this point resulted in a straigthening of the MWCNT sheet accompanied by a deformation of 50%; and, as a result, the resistance of the MWCNT sheet rapidly increased (Figure 4b), which resulted in a decrease in the PCE. At the same time, the fiber-shaped PSC cannot be returned to its original structure after releasing the tensile force, as the deformation of the spring-like Ti wire was not reversible upon stretching beyond 30%. When stretching the fiber-shaped PSC to 80%, the MWCNT sheet was destroyed, and the fiber-shaped PSC failed to work. Therefore, an effective strain of 30% was determined for these fiber-shaped PSC.







Figure 5. a,b) A stretchable PSC textile being integrated into clothes. c) Dependence of energy-conversion efficiency on bending cycle number. η_0 and η correspond to the energy-conversion efficiencies before and after bending, respectively (the inserted image schematically shows the bending process). d) Dependence of energy-conversion efficiency on the stretching cycle number. η_0 and η correspond to the energy-conversion efficiencies before and after bending, respectively (the inserted image schematically shows the bending before and after stretching for different cycles, respectively (the inserted image schematically shows the stretching process).

The maximal strain can be further increased, however, to over 100% by increasing the thickness of the MWCNT sheet. However, a thicker MWCNT sheet will largely decreases the optical transmittance, leading to a decrease in the PCE.^[19] More efforts are required to increase the reversible deformation capability of the spring-like metal wire to achieve a higher stretchability.

The fiber-shaped PSCs were then woven into PSC textiles without the need for sealing (Figure 5a,b). The PCE of the fiber-shaped PSC could be maintained at about 90% after it was bent for 1000 times (Figure S15, Supporting Information), whereas conventional planar PSCs usually show a much larger decrease in PCE after bending.^[20-22] From the woven textiles we produced clothes that were also flexible and stretchable, and their PCE also was retained at about 90% after they had been bent for 1000 times (Figure 5c). Figure 5d compares the PCEs before and after stretching by 30% for 50 cycles, and the PCE values changed less than 10%. Figure S16 in the Supporting Information shows the voltage dependence on the number of PSCs after they were woven into clothes. Importantly, the produced voltage is continuously enhanced with more one-dimensional PSCs that are arranged in series, so they can be effectively scaled up for various practical applications, for instance, electronic cells for wearable and portable products in mimicking the textile industry.

To summarize, an effective and low-cost route has been designed to develop novel PSC fibers and textiles that are both highly flexible and stretchable. They show stable energy-conversion efficiencies with a slight variation after bending and stretching for many cycles. These PSC fibers and textiles are also lightweight and stable, a necessity in the advancement of a broad spectrum of electronic products in the near future.^[23,24]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by MOST (2011CB932503), NSFC (21225417), STCSM (12nm0503200), the Fok Ying Tong Education Foundation, the Program for Special Appointments of Professors at Shanghai Institutions of Higher Learning, and the Program for Outstanding Young Scholars from the Organization Department of the CPC Central Committee.

- [2] Y. Li, Y. Zou, Adv. Mater. 2008, 20, 2952.
- [3] S.-I. Na, S.-S. Kim, J. Jo, D.-Y. Kim, Adv. Mater. 2008, 20, 4061.
- [4] F. C. Krebs, M. Jørgensen, K. Norrman, O. Hagemann, J. Alstrup, T. D. Nielsen, J. Fyenbo, K. Larsen, J. Kristensen, *Sol. Energy Mater. Sol. Cells* 2009, 93, 422.
- [5] T. T. Larsen-Olsen, F. Machui, B. Lechene, S. Berny, D. Angmo, R. Søndergaard, N. Blouin, W. Mitchell, S. Tierney, T. Cull, P. Tiwana, F. Meyer, M. Carrasco-Orozco, A. Scheel, W. Lövenich,

^[1] S. K. Hau, H.-L. Yip, N. S. Baek, J. Zou, K. O'Malley, A. K. Y. Jen, *Appl. Phys. Lett.* **2008**, *92*, 253 301.

communications



- [6] P. Lee, J. Lee, H. Lee, J. Yeo, S. Hong, K. H. Nam, D. Lee, S. S. Lee, S. H. Ko, Adv. Mater. 2012, 24, 3326.
- [7] J.-F. Salinas, H.-L. Yip, C.-C. Chueh, C.-Z. Li, J.-L. Maldonado, A. K. Y. Jen, Adv. Mater. 2012, 24, 6362.
- [8] M. Kaltenbrunner, M. S. White, E. D. Glowacki, T. Sekitani, T. Someya, N. S. Sariciftci, S. Bauer, *Nat. Commun.* 2012, *3*, 770.
- [9] M. R. Lee, R. D. Eckert, K. Forberich, G. Dennler, C. J. Brabec, R. A. Gaudiana, *Science* 2009, 324, 232.
- [10] D. Liu, M. Zhao, Y. Li, Z. Bian, L. Zhang, Y. Shang, X. Xia, S. Zhang, D. Yun, Z. Liu, A. Cao, C. Huang, *ACS Nano* **2012**, *6*, 11 027.
- [11] a) X. Sun, W. Wang, L. Qiu, W. Guo, Y. Yu, H. Peng, Angew. Chem. Int. Ed. 2012, 51, 8520; b) L. Qiu, X. Sun, Z. Yang, W. Guo, H. Peng, Acta Chim. Sinica 2012, 70, 1523; c) Z. Yang, J. Deng, X. Sun, H. Li, H. Peng, Adv. Mater. 2014, 26, 2643; d) S. Pan, Z. Yang, H. Li, L. Qiu, H. Sun, H. Peng, J. Am. Chem. Soc. 2013, 135, 10622; e) Z. Zhang, Z. Yang, Z. Wu, G. Guan, S. Pan, Y. Zhang, H. Li, J. Deng, B. Sun, H. Peng, Adv. Energy Mater. 2014, DOI: 10.1002/aenm.201301750.
- [12] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes, *Nano Lett.* **2006**, *6*, 215.
- [13] T. Chen, L. Qiu, H. Li, H. Peng, J. Mater. Chem. 2012, 22, 23 655.
- [14] Z. Zhang, X. Chen, P. Chen, G. Guan, L. Qiu, H. Lin, Z. Yang, W. Bai, Y. Luo, H. Peng, *Adv. Mater.* **2014**, *26*, 466.

- [15] J. Akilavasan, K. Wijeratne, H. Moutinho, M. Al-Jassim, A. R. M. Alamoud, R. M. G. Rajapakse, J. Bandara, J. Mater. Chem. A 2013, 1, 5377.
- [16] M. Ye, X. Xin, C. Lin, Z. Lin, Nano Lett. 2011, 11, 3214.
- [17] K. Lim, S. Jung, J.-K. Kim, J.-W. Kang, J.-H. Kim, S.-H. Choa, D.-G. Kim, Sol. Energy Mater. Sol. Cells 2013, 115, 71.
- [18] T. Chen, S. Wang, Z. Yang, Q. Feng, X. Sun, L. Li, Z. Wang, H. Peng, Angew. Chem. Int. Ed. 2011, 50, 1815.
- [19] Z. Yang, J. Deng, X. Chen, J. Ren, H. Peng, Angew. Chem. Int. Ed. 2013, 52, 13 453.
- [20] K. Aitola, M. Borghei, A. Kaskela, E. Kemppainen, A. G. Nasibulin, E. I. Kauppinen, P. D. Lund, V. Ruiz, J. Halme, *J. Electroanal. Chem.* 2012, 683, 70.
- [21] Y. Leterrier, L. Médico, F. Demarco, J. A. E. Månson, U. Betz, M. F. Escolà, M. Kharrazi Olsson, F. Atamny, *Thin Solid Films* 2004, 460, 156.
- [22] L. Yang, T. Zhang, H. Zhou, S. C. Price, B. J. Wiley, W. You, ACS Appl. Mater. Interfaces 2011, 3, 4075.
- [23] D.-H. Kim, J. A. Rogers, Adv. Mater. 2008, 20, 4887.
- [24] Y.-H. Lee, J.-S. Kim, J. Noh, I. Lee, H. J. Kim, S. Choi, J. Seo, S. Jeon, T.-S. Kim, J.-Y. Lee, J. W. Choi, *Nano Lett.* **2013**, *13*, 5753.

Received: March 31, 2014 Revised: August 26, 2014 Published online: September 18, 2014

