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Supporting Information

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Stretchable Polymer Solar Cell Fibers

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Supplementary Information

Experimental section

Spinnable multi-walled carbon nanotube (MWCNT) arrays were synthesized by the chemical vapour deposition with Fe (1.2 nm)/Al_2O_3 (3 nm) on a silicon substrate used as the catalyst at 740 ℃. Ethylene was used as the carbon source, and a gas mixture of H_2 and Ar was used as the carrier gas. The flow rates of H_2, Ar and C_2H_4 were 30, 400 and 90 sccm, respectively. The MWCNT arrays with a thickness of 230 μm had been mainly used in this work.

The detailed preparation of the spring-like working electrode is described below. A Ti wire (diameter 127 μm and purity 99.9%) was wound onto a steel wire with a diameter of 600 μm, followed by removal from the steel wire to form a spring-like shape. The aligned TiO_2 nanotubes arrays were grown onto the surface of the Ti wire by an electrochemical anodization method in 0.3 wt% NH_4F/ethylene glycol solution containing 8 wt% H_2O at voltages of 60 V for 10 min. The anodization was performed in a two-electrode electrochemical cell with a Ti wire and Pt sheet as the anode and cathode, respectively.[S1,S2] The resulting wires were washed with deionized water to remove the electrolyte, followed by annealing at 500 ℃ for 1 h in air. The polymer layers were dip-coated onto the modified Ti wire. Typically, the modified Ti wire was infiltrated into a mixture solution of P3HT (concentration of 30 mg/mL) and PCBM (concentration of 24 mg/mL) in chlorobenzene in a glove box.[S3] The resulting Ti wire was taken out of the solution and annealed at 150 ^{o}C for 10 min. A mixture of PEDOT:PSS aqueous solution (PH1000) and 2-propanol with a volume ratio of 4/1 was further coated on the outer surface. The treated Ti wire was also taken out for annealing at 150 ^{o}C for 10 min.

After formation of the spring-like working electrode, an elastic rubber fiber was then inserted into it. The aligned MWCNT sheet was finally wound on the modified spring-like Ti wire to form the stretchable fiber-shaped PSC. The stability of the fiber-shaped PSC was performed in air and argon.

The calculation of the energy conversion efficiency is summarized below.[S4] The fiber-shaped PSC was illuminated under the solar simulator with the incident light at the top. As widely recognized, the effective area of the working electrode was calculated as the projected area. Figure S17 shows the detailed calculation process. The entire projected area of the working electrode in the x-axis direction is shown in

Figure S17b, and the effective area of the working electrode can be then obtained after subtracting the black area which was shadowed by the elastic fiber (Figure S17c).

The working electrode exhibits a three-dimensional helical structure and can be mathematically expressed as X = A$\cos t$, Y = A$\sin t$, and Z = Bt. The spring-like working electrode is fabricated by winding the Ti wire (127 μm) on a steel wire with a diameter of 600 μm. Therefore, the amplitude A can be calculated to be 364 μm. B is a constant and may be obtained from the pitch distance of 560 μm, i.e., 2πB = 560 μm. B is calculated as 89 μm. Therefore, the projected area of the working electrode in the x-axis direction is expressed as $Y = 364\sin\frac{\pi Z}{280}$. For the working electrode, the arc length (L) can be calculated by the equation $L = \int\sqrt{1+(\frac{dY}{dZ})^2}\,dZ$, so $L = \int\sqrt{1+(\frac{364\pi}{280}\cos\frac{\pi Z}{280})^2}\,dZ$. In the case of a pitch including the shaded part, $L_1 = \int_0^{560}\sqrt{1+(\frac{364\pi}{280}\cos\frac{\pi Z}{280})^2}\,dZ$ = 1599 μm. For the shaded part, Z is calculated to be 65 at Y of 250 μm according to $Y = 375\sin\frac{\pi Z}{280}$. Therefore, the arc length is obtained by $L_2 = \int_{-65}^{65}\sqrt{1+(\frac{364\pi}{280}\cos\frac{\pi Z}{280})^2}\,dZ$ = 502 μm. Finally, the effective area (S) of the working electrode $S = n \times D \times (L_1 - L_2)$, where n and D correspond to the cycle number and diameter of the working electrode (127 μm), respectively. Therefore, S = n × 127 × (1,599 - 502) = n × 139,319 μm^2.

The optical micrograph was obtained from Olympus BX51. The structures were characterized by scanning electron microscopy (Hitachi FE-SEM S-4800 operated at 1 kV). The photoelectric conversion was characterized by recording J-V curves with a Keithley 2400 Source Meter under illumination (100 mW/cm^2) of simulated AM 1.5 solar light coming from a solar simulator (Oriel-Sol3A 94023 A equipped with a 450W Xe lamp and an AM1.5 filter).

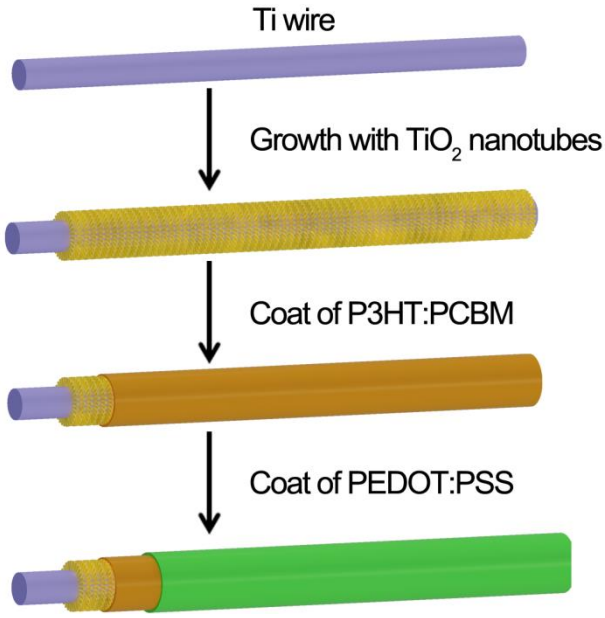

Figure S1. Schematic illustration to the modification of the Ti wire and the coat of photoactive materials. Aligned TiO_2 nanotubes were perpendicularly grown on the Ti wire by electrochemical anodization, followed by sequential coat of P3HT:PCBM and PEDOT:PSS layers.

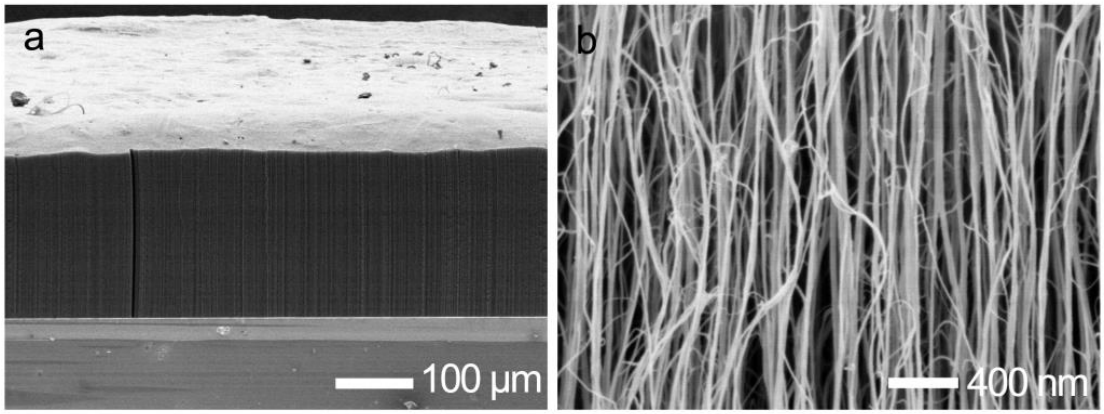

Figure S2. Scanning electron microscopy (SEM) image of a spinnable array at low (**a**) and high (**b**) magnifications, respectively.

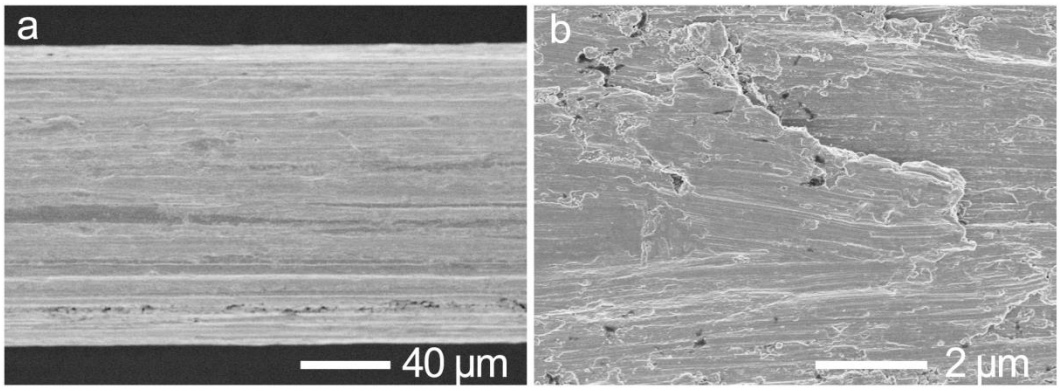

Figure S3. SEM images of a bare Ti wire at low (**a**) and high (**b**) magnifications.

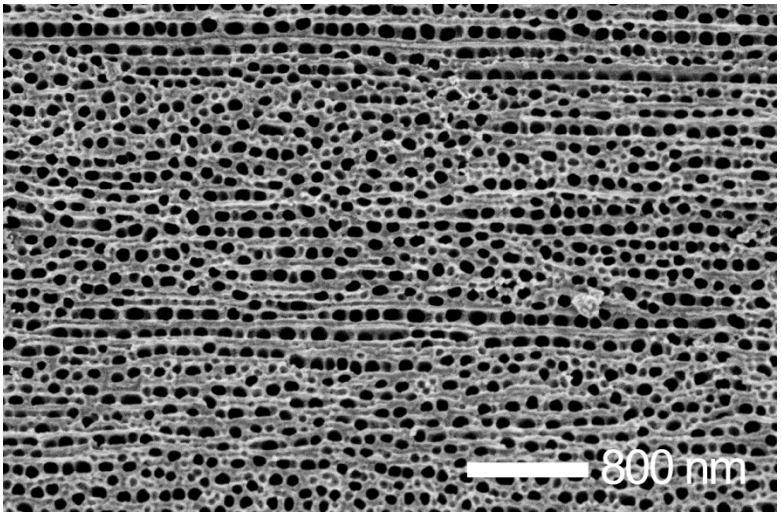

Figure S4. SEM image of the aligned TiO_2 nanotubes.

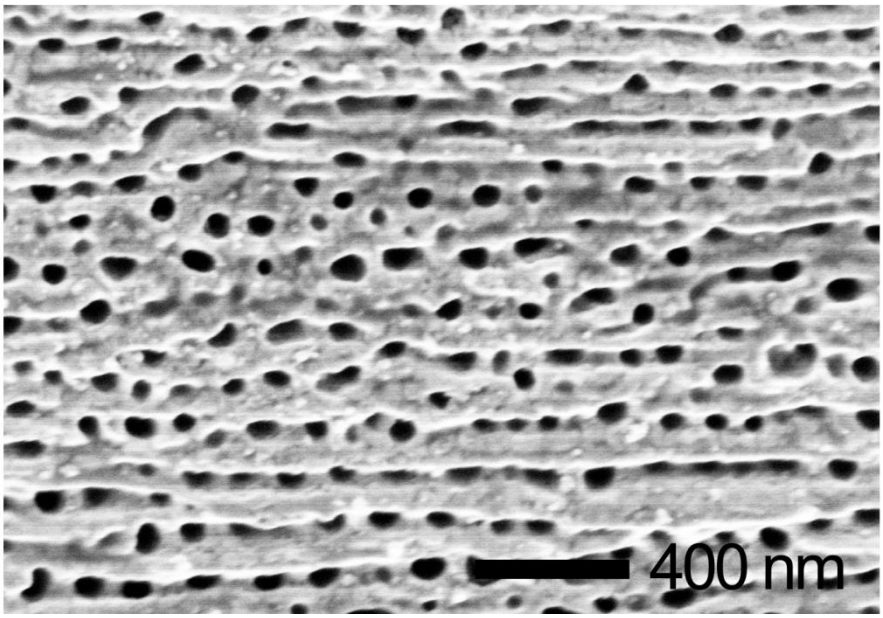

Figure S5. P3HT:PCBM layer coated on the modified Ti wire by a top view.

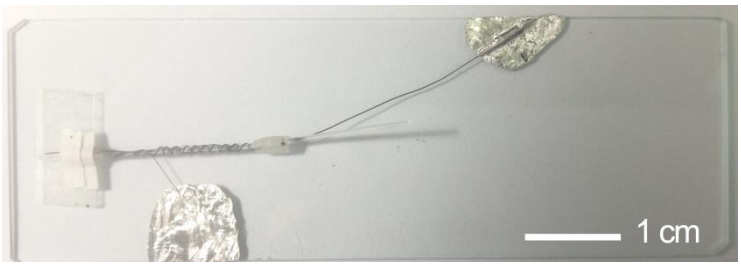

Figure S6. Photograph of a stretchable fiber-shaped PSC stabilized on a glass slide.

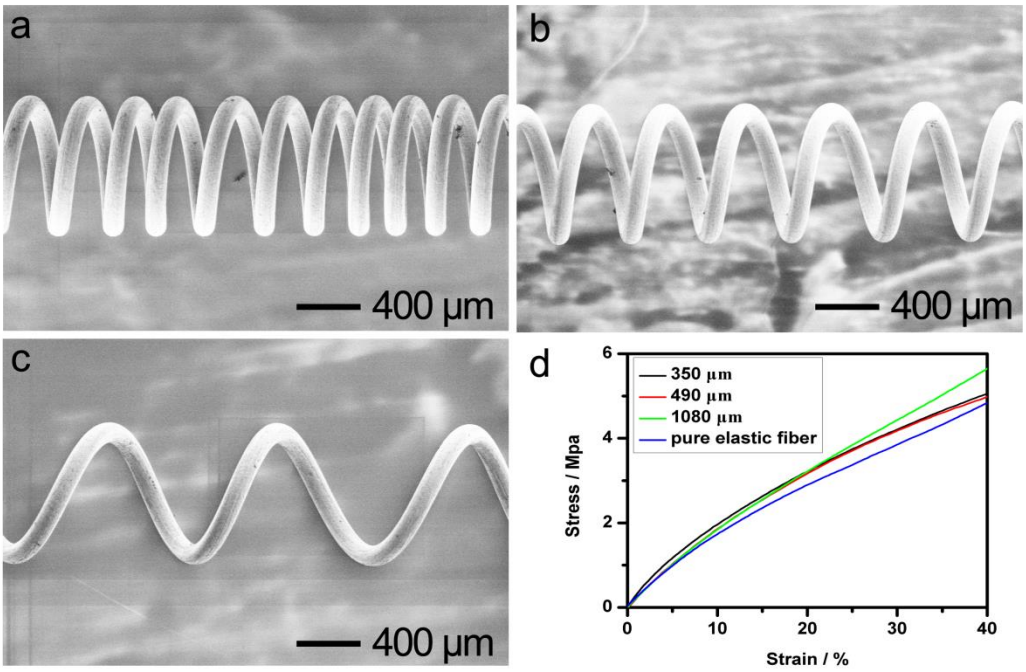

Figure S7. a, b and **c.** SEM images of a spring-like Ti wire with increasing pitch distances from 350 and 490 to 1080 μm, respectively. **d**. Comparison of stress-strain curves between the pure elastic fiber and stretchable PSCs with pitch distances of 350, 490 and 1080 μm.

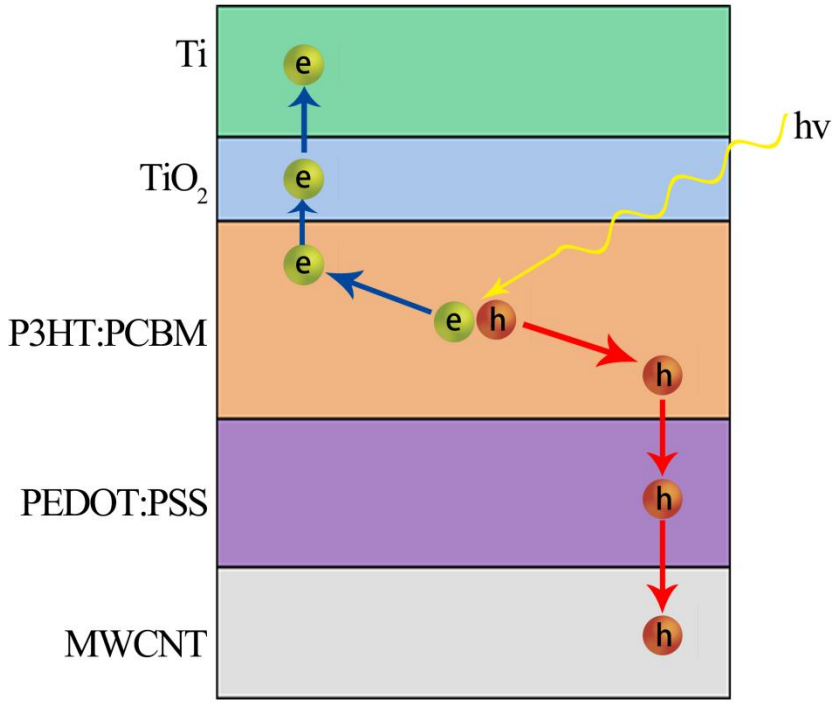

Figure S8. Schematic illustration to the mechanism of the stretchable fiber-shaped PSC.

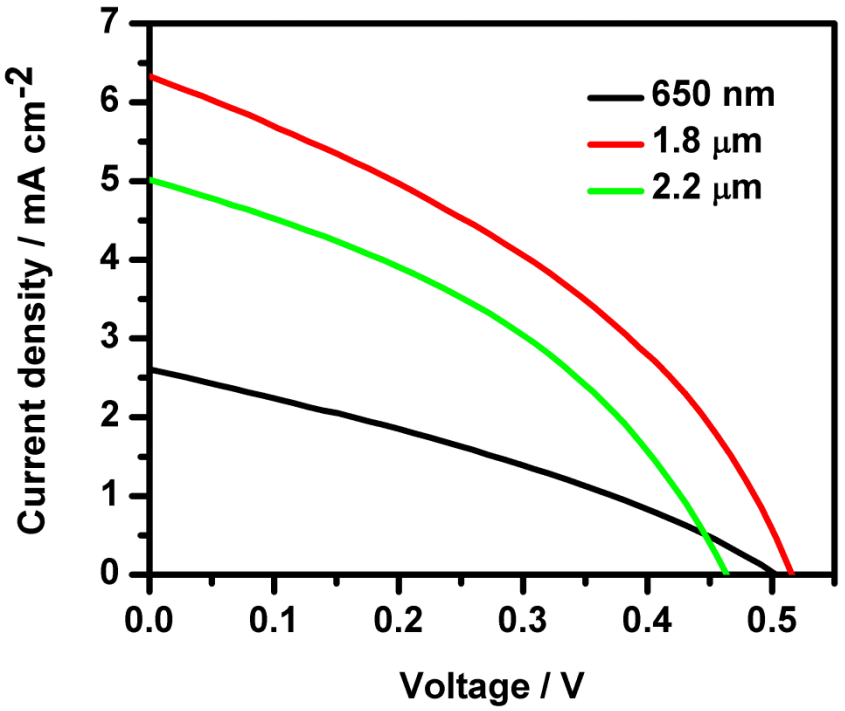

Figure S9. J-V curves of fiber-shaped PSCs based on TiO_2 nanotubes with lengths of 650 nm, 1.8 μm and 2.2 μm.

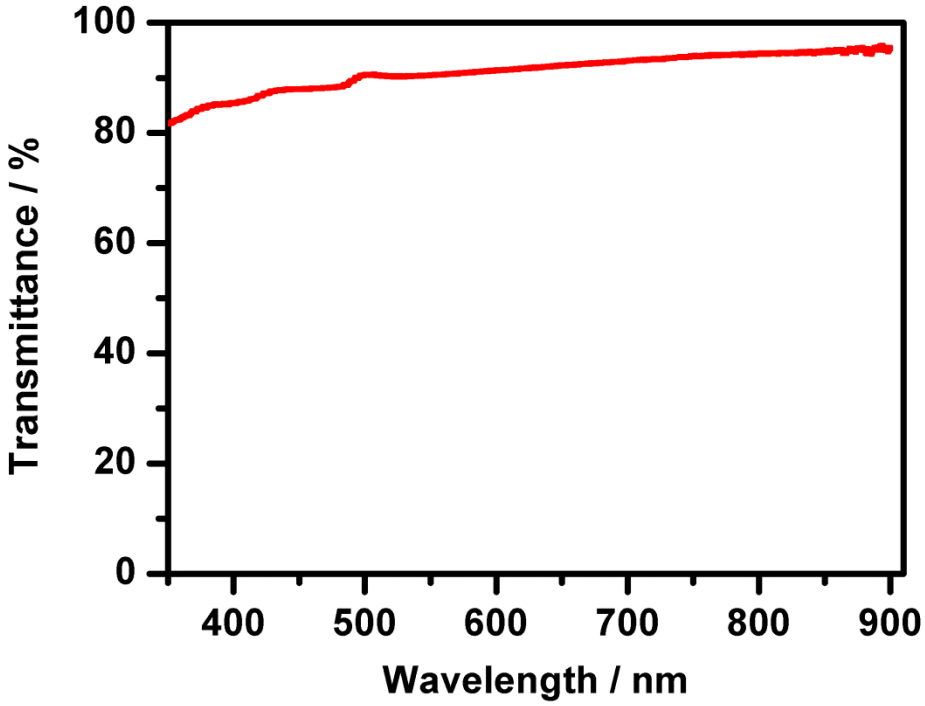

Figure S10. Optical transmittance spectra for a layer of MWCNT sheet.

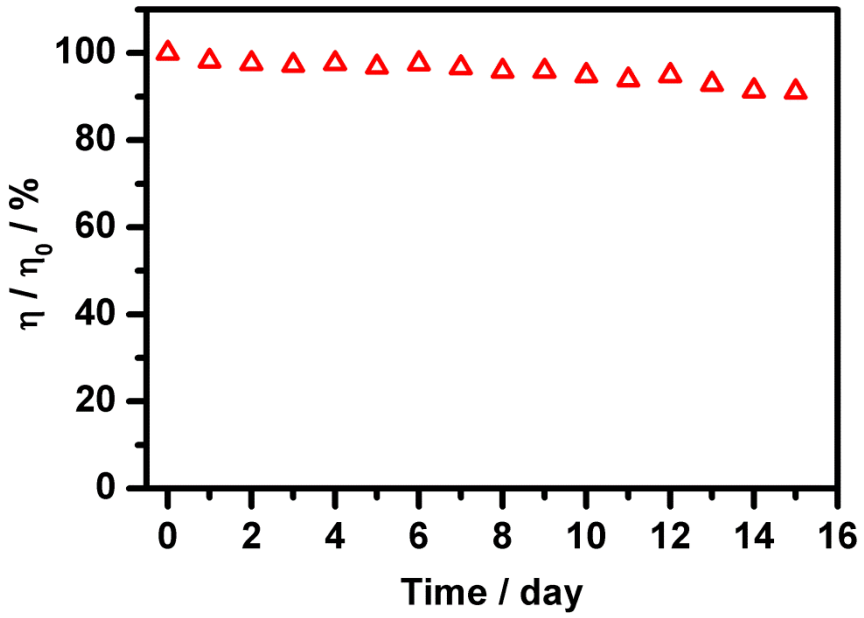

Figure S11. Dependence of energy conversion efficiency of a fiber-shaped PSC on time.

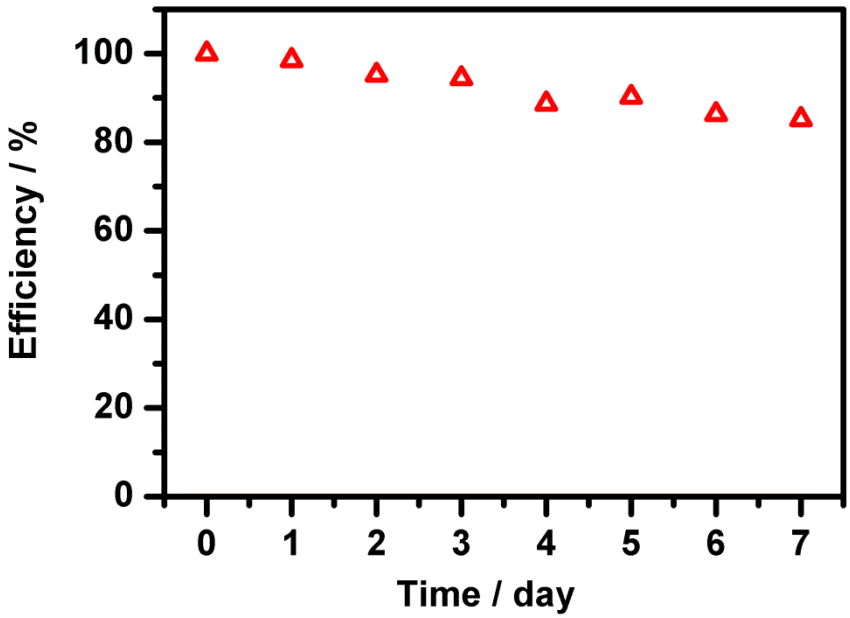

Figure S12. Dependence of the energy conversion efficiency of fiber-shaped PSC on the time in air for a period of a week.

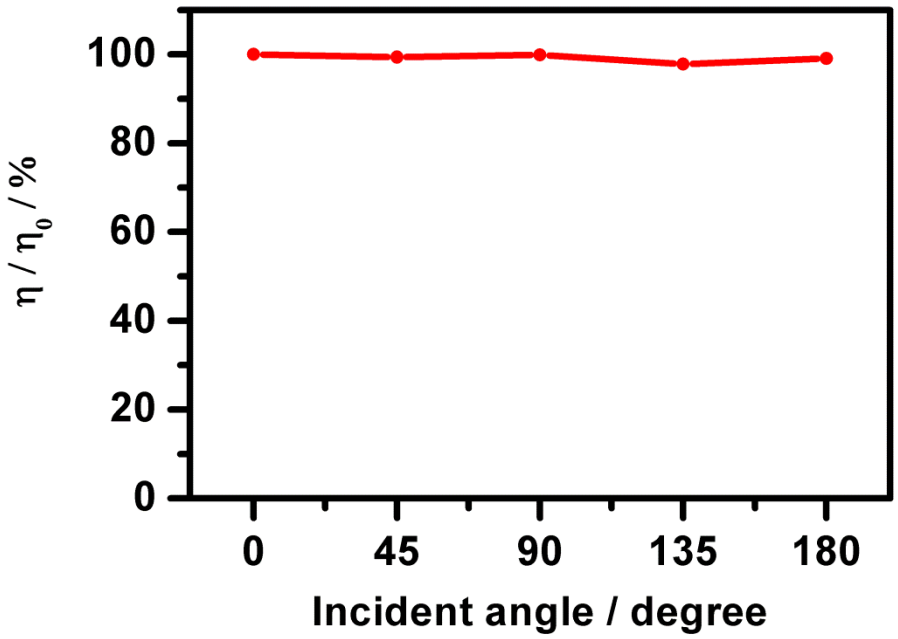

Figure S13. Dependence of energy conversion efficiency on incident angle of the light. η_0 and η correspond to the energy conversion efficiencies at 0 and the other degree, respectively.

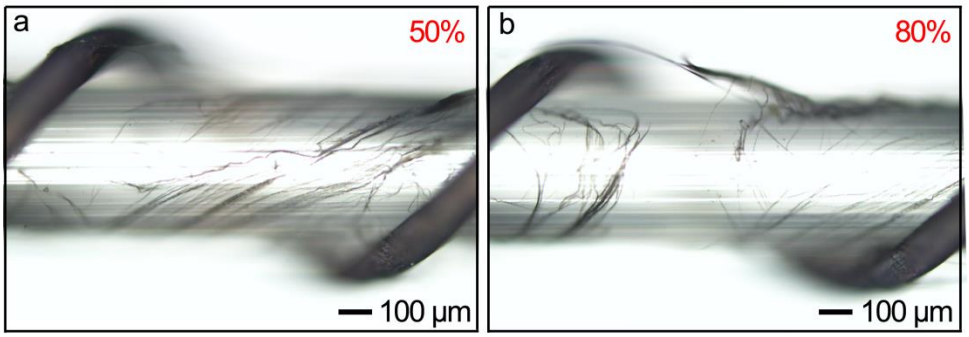

Figure S14. Photographs of a stretchable fiber-shaped PSC at strains of 50% (a) and 80% (b).

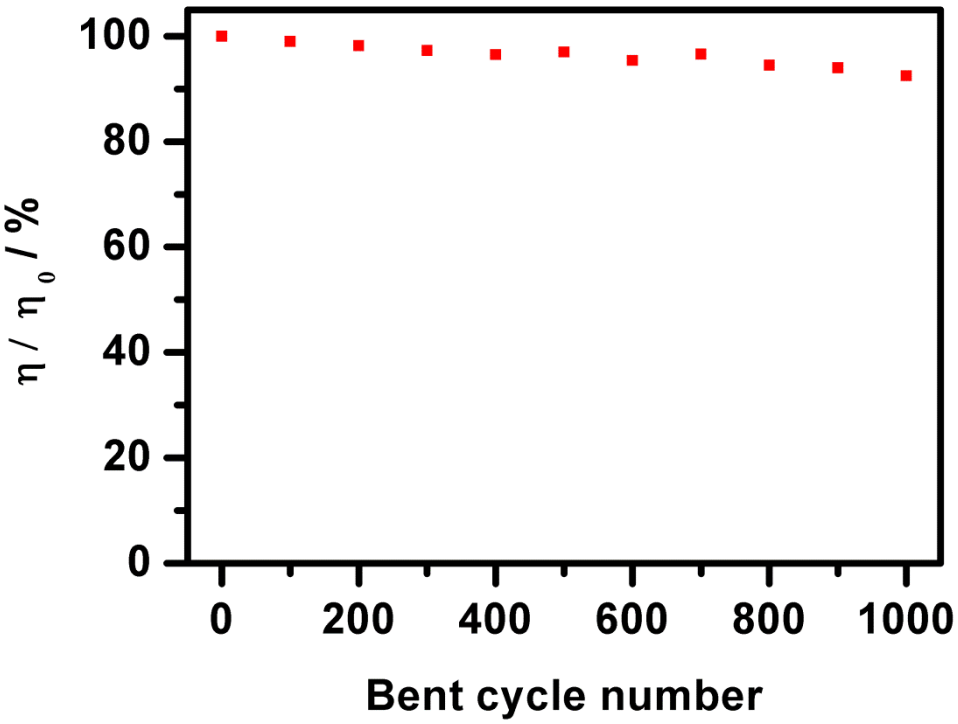

Figure S15. Dependence of energy conversion efficiency on bent cycle number. η_0 and η correspond to the efficiencies before and after bending, respectively.

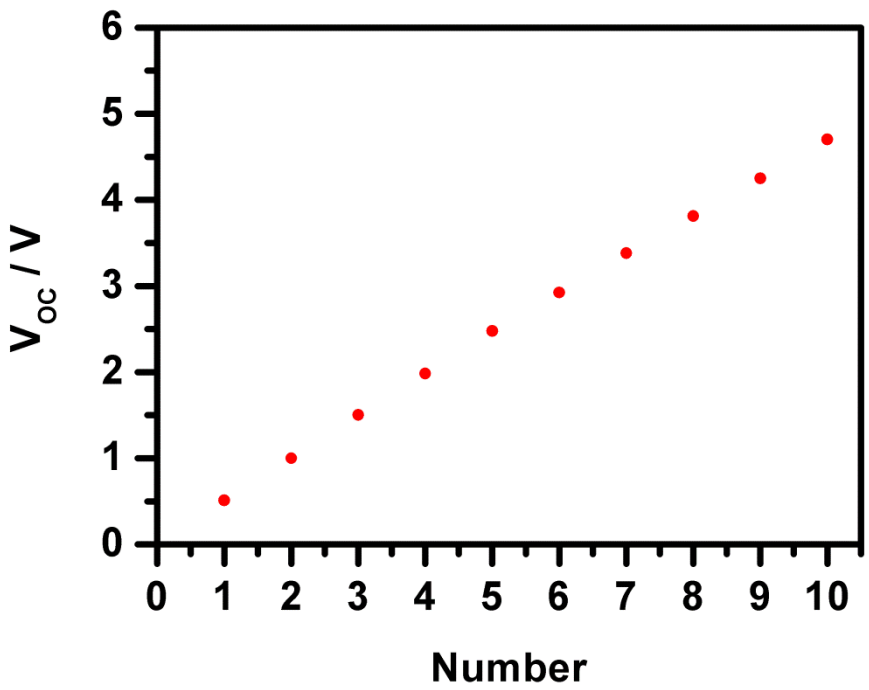

Figure S16. Dependence of voltage on the number of fiber-shaped PSCs that are connected in series in a textile.

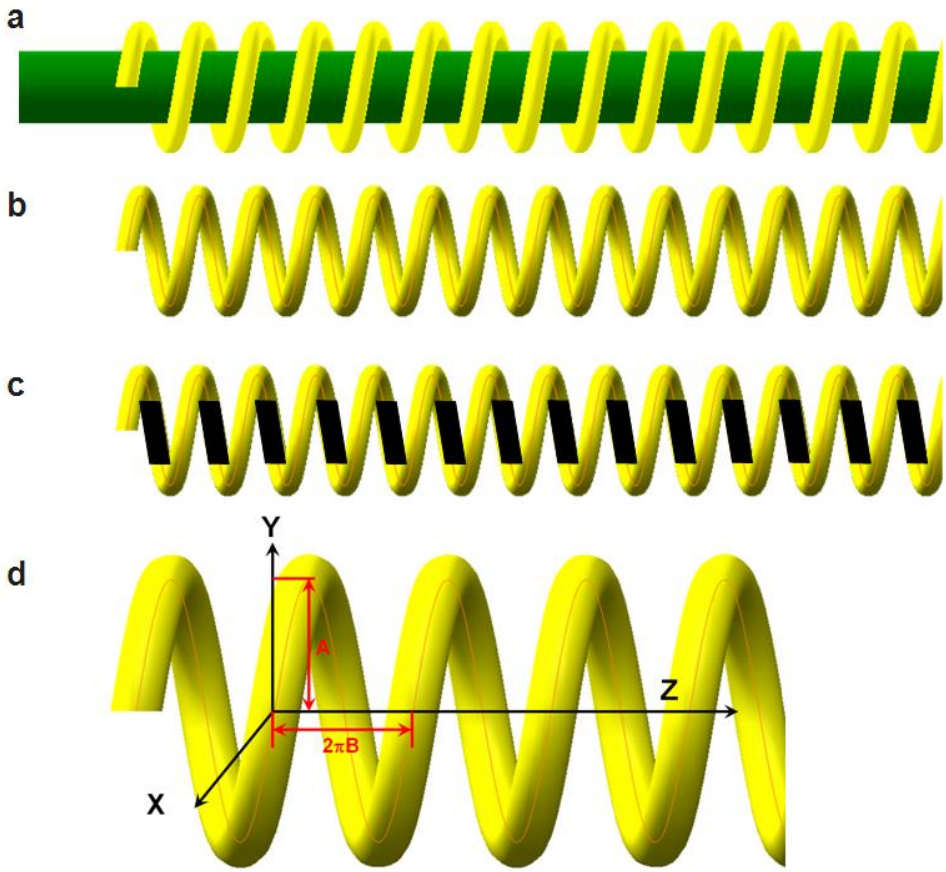

Figure S17. Schematic illustration to the calculation of the effective area.

References for the Supporting Information

[S1] O. K. Varghese, M. Paulose, C. A. Grimes, *Nat. Nanotechnol.* **2009**, *4*, 592.

[S2] J. H. Yun, Y. H. Ng, C. Ye, A. J. Mozer, G. G. Wallace, R. Amal, *ACS Appl. Mater. Inter.* **2011**, *3*, 1585.

[S3] 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*, 11027.

[S4] Z. Yang, J. Deng, X. Sun, H. Li, H. Peng, *Adv. Mater.* **2014**, *26*, 2643.