

† Electronic Supplementary Information

Preparation of conductive thread: A commercial thread (Φ ca. 300 μm) was cleaned by acetone and dried at 120 $^{\circ}\text{C}$ in air. It was quickly dipped into 5 wt% DMSO doping commercial PEDOT:PSS aqueous solution (CLEVIOS PH 1000), taken out, and then heated for 10 min at 120 $^{\circ}\text{C}$. This process was repeated desirable times. Then conductive thread was obtained. PEDOT:PSS loading on the thread was obtained by measuring the weight gain of the thread per centimeter due to coated PEDOT:PSS with analytical balance (Mettler Toledo XS105 DU, readability 0.01 mg).

Solvent treatment of conductive thread: the 5-cm-length conductive threads as prepared were soaked in 1 mL of deionized water, acetonitrile and an acetonitrile solution containing I^-/I_3^- , respectively. The conductive thread soaked in electrolyte was washed with acetonitrile several times to remove solutes before dried in air. Other two threads were dried directly in air.

Preparation of fiber photoanode: Fiber photoanodes were prepared as we reported before.¹⁴ In briefly, after cleaning with acetone, isopropanol, and methanol, Ti wires (Φ 250 μm , Alfa Aesar) were dipped into the TiO_2 colloid, taken out, and then heated for 5 min at 400 $^{\circ}\text{C}$. This process was repeated until the thickness of the TiO_2 porous film reached 10 μm . After pre-treating with fresh TiCl_4 solution (40 mM) for 12 h, the wires was sintered in air at 450 $^{\circ}\text{C}$ for 30 min, and immersed into N719 ethanol solution (0.5 mM) for 24 h.

Assembly of fiber-shaped DSSC: A conductive thread and a photoanode were parallel inserted into a glass capillary (internal diameter: Φ 0.9 mm, external diameter: Φ 1.2 mm) filled with the electrolyte (acetonitrile solution containing 0.04 M I_2 , 0.6 M BMII, 0.05 M GSCN, 0.05 M LiClO_4 , and 0.3 M TBP). The capillary was sealed with paraffin at both ends to attain Fiber-shaped DSSCs.

Scanning electron microscopy (S-4800 Hitachi) was used to observed the sample morphology. The resistance R of the thread with a length L and diameter Φ are measured by Multimeter 2000 (Keithley) using two-probe method, and the conductivity σ could be easily calculated by $\sigma = 4L/(\pi R \Phi^2)$. Cyclic voltammetry was conducted on a CHI electrochemical workstation (Shanghai Chenhua) with a 1.5 cm-long fibrous conductive thread or 0.36 mm^2 Pt sheet as the working electrode, platinum sheets as the CE, and Ag/AgCl as the reference electrode in an acetonitrile solution containing I_2 (0.4 mM), BMII (6 mM), and LiClO_4 (0.1 M). YSS-50A simulated solar source (Yamashita DESO, 100 mW/cm²) was used for photovoltaic test. The effective illumination area of fiber-shaped DSSCs was taken as projected area of photoanode. Electrochemical workstation (AUTOLAB PG30) was used to character the electrochemical impedance of the DSSC under dark condition, a forward bias of 680 mV, a perturbation voltage of 5 mV, and a frequency range of 300 kHz–10 mHz.