† Electronic Supplementary Information

The TiO_2 colloid was prepared as following: Acetic acid (1 mL), tetrabutyl titanate (6 ml), deionized water (30 mL), and nitric acid (0.25 mL, 65%–68%) were mixed, stirred and then heated for 2 h

- s at 80 °C to form a translucent solution. After 12 h of hydrothermal reaction at 220 °C, two-thirds of the solvent was evaporated. The precipitate was dispersed in the remaining solvent by stirring, followed by dissolving 2.6 g polyethylene glycol (Mw=20,000). This yielded a final TiO₂ colloid. Ti wire (Φ 250 μm, Alfa Aesar)
- ¹⁰ was chosen as the substrate for fiber-shaped WE, considering good conductivity of Ti metal as well as Ti/TiO₂ interface which favors electron transfer from TiO₂ to Ti substrate. After cleaning with acetone, isopropanol, and methanol in order, Ti wire was heated for about 10 min at 400 °C. It was quickly dipped into the
- ¹⁵ TiO₂ colloid, taken out, and then heated for 5 min at 400 °C. This process was repeated about 20 times until the thickness of the TiO₂ porous film around the wire was 10–15 μ m. The as-prepared wire was pre-treated with fresh TiCl₄ solution (40 mM) for 12 h, the wire was again sintered in air at 450 °C for 30 min, cooled to
- ²⁰ 380 °C and then immediately immersed into N719 ethanol solution (0.5 mM) for 24 h.

A bundle of CF (Toray M40J) was first soaked in acetone for 50 min and then in 1.5 M sulfuric acid solution containing 0.55 M $(NH_4)_2S_2O_8$ for 1 h. It was subsequently washed with deionized

²⁵ water and dried in air. The pre-treated CF was arranged evenly on a glass substrate and then platinized through magnetron sputtering (JCP-200). The CEs were prepared by wringing a small amount of the CF into thin bundles with different diameters. Composite CEs were obtained by twisting a CF bundle with two ³⁰ stainless steel wires (Φ 40 μ m).

The CF-based CEs or Pt wire (Φ 40 µm) were twisted around the working electrode (4 cm long) ten times and then inserted into a glass capillary (internal diameter: Φ 0.9 mm, external diameter: Φ 1.2 mm) filled with an acetonitrile solution containing I₂ (0.04

³⁵ M), BMII (0.6 M), GSCN (0.05 M), LiClO₄ (0.05 M), and TBP (0.3 M). Fiber-shaped DSSCs was obtained after sealing the capillary with paraffin at both ends.

The morphology of the CE was observed by scanning electron microscopy (SEM) (S-4800 Hitachi). The catalytic activity of the

- ⁴⁰ CE materials was characterized by cyclic voltammetry on a CHI electrochemical workstation (Shanghai Chenhua) with a 1.5 cmlong fibrous CF-based electrode or 0.36 mm² Pt sheet as the working electrode, platinum sheets as the CE, and Ag/AgCl as the reference electrode in an acetonitrile solution containing I₂
- ⁴⁵ (0.4 mM), BMII (6 mM), and LiClO₄ (0.1 M). The simulated solar light source used for the IV tests came from an YSS-50A instrument (Yamashita DESO), and the light intensity was 100 mWcm⁻². The effective illumination area of fiber-shaped DSSCs was taken as its length multiplied by the diameter of WE, which
- ⁵⁰ is the projected area of the electrodes. The electrochemical impedance of the DSSC was tested by an electrochemical workstation (AUTOLAB PG30) under dark condition, a forward bias of 680 mV, a perturbation voltage of 5 mV, and a frequency range of 400 kHz–50 mHz.



Fig. S1 SEM images of CF (a) and Pt-CF (b)





Fig. S3 EIS curve of the fiber-shaped DSSC with a 100- μ mdiameter Pt wire CE under dark condition. The inset shows the equivalent EIS circuit for the fiber-shaped DSSC, where R_s is the 65 ohmic serial resistance, CPE is the constant phase element, R_{CT,CE} is the charge-transfer resistance of the CE/electrolyte interface, and R_{CT,WE} is the electron recombination resistance of the working electrode/electrolyte inteface.