The TiO\textsubscript{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 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 TiO\textsubscript{2} colloid. Ti wire (Φ 250 µm, Alfa Aesar) was chosen as the substrate for fiber-shaped WE, considering good conductivity of Ti metal as well as Ti/TiO\textsubscript{2} interface which favors electron transfer from TiO\textsubscript{2} 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 TiO\textsubscript{2} colloid, taken out, and then heated for 5 min at 400°C. This process was repeated about 20 times until the thickness of the TiO\textsubscript{2} porous film around the wire was 10–15µm. The as-prepared wire was pre-treated with fresh TiCl\textsubscript{4} solution (40 mM) for 12 h, the wire was again sintered in air at 450°C for 30 min, cooled to 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\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} for 1 h. It was subsequently washed with deionized 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 stainless steel wires (Φ 40 µm).

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 I\textsubscript{2} (0.04 M), BMII (0.6 M), GSCN (0.05 M), LiClO\textsubscript{4} (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 CE materials was characterized by cyclic voltammetry on a CHI electrochemical workstation (Shanghai Chenhua) with a 1.5 cm-long fibrous CF-based electrode or 0.36 mm\textsuperscript{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\textsubscript{2} (0.4 mM), BMII (6 mM), and LiClO\textsubscript{4} (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\textsuperscript{-2}. The effective illumination area of fiber-shaped DSSCs was taken as its length multiplied by the diameter of WE, which 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.