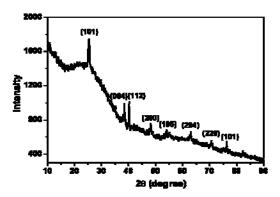
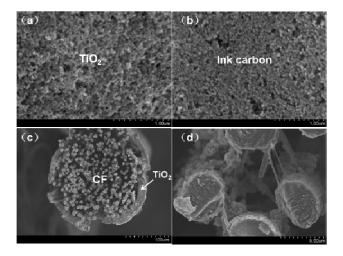
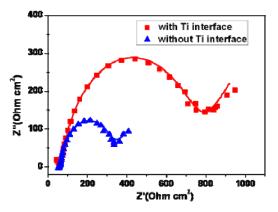
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/



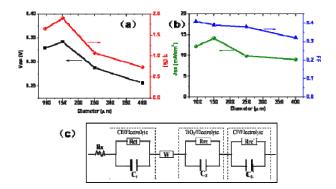
**Fig.S1** XRD characteristic of the annealed TiO<sub>2</sub> film after calcination in a muffle furnace at 400°C for 40 min. The XRD spectrum shows an anatase structure (the peak at the 25.3° scattering angle can be indexed to the (101) plane of the anatase TiO<sub>2</sub>).



**Fig.S2** (a) The morphology of the TiO<sub>2</sub> layer shows a porous and interconnected nanoparticle structure. (b) Morphology of the ink carbon layer coating on the surface of CE under higher resolution. (c) A complete cross-section view of the CF/TiO<sub>2</sub> photoanode. (d) SEM image of carbon fiber monofilaments connected by TiO<sub>2</sub> clusters in the core of the CF/TiO<sub>2</sub> photoanode.



**Fig.S3** EIS curves of fiber-shaped DSSCs based on the CF/TiO<sub>2</sub> photoanode with ( $D_{\text{CF/Ti/TiO2}}$ ) or without ( $D_{\text{CF/Ti/TiO2}}$ ) Ti interface layer. EIS were measured using a Solartron 1250 frequency analyzer under dark conditions and 0.3 V forward bias. The perturbation voltage was 10 mV and the frequency range was from 65.5 kHz to 50 mHz. The recombination resistance ( $R_{re}$ ) at the working electrode /electrolyte interface can characterize the degree of recombination, corresponding to the diameter of the second semicircle in the plot. Higher  $R_{re}$  value means it is more difficult for the electrons in the TiO<sub>2</sub> film to recombine with oxidative species in the electrolyte. The  $R_{re}$  for  $D_{\text{CF/Ti/TiO2}}$  and  $D_{\text{CF/TiO2}}$  are 655 and 248.6  $\Omega$  cm<sup>2</sup>, respectively.



**Fig.S4** (a) Change in the power conversion efficiency (η) and open-circuit voltage ( $V_{oc}$ ) and (b) fill factor (FF) and short-circuit current density ( $J_{sc}$ ) as the photoanode diameter increases from 95 to 400 μm. (c) Equivalent circuit of the all-carbon electrode-based fiber-shaped DSSCs based on the CF/TiO<sub>2</sub> photoanode with different diameters. From left to right— $R_s$ : serial resistance;  $R_{ct}$ : charge transfer resistance of the CE/electrolyte interface;  $C_1$ : capacitance of the counter electrode;  $R_{re}$ : recombination resistance of the TiO<sub>2</sub>/electrolyte interface;  $C_2$ : capacitance of the TiO<sub>2</sub> surface;  $R_{re}$ : recombination resistance of the carbon fiber/electrolyte interface in photoanode;  $C_2$ ': capacitance of the CF surface; and W: diffusion resistance of the electrolyte.