

## Supporting Information

### Composite of TiO<sub>2</sub> Nanofibers and Nanoparticles for Dye Sensitized Solar Cells with Significantly Improved Efficiency

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#### 1. Electrospun TiO<sub>2</sub> nanofibers

**Materials.** Titanium (IV) *n*-butoxide (TNBT), polyvinylpyrrolidone (PVP, M<sub>w</sub> = 1,300,000), *N,N*-dimethylformamide (DMF, anhydrous), isopropanol (IPA, anhydrous), and acetic acid (HAc, glacial) were purchased from the Sigma-Aldrich Co. (Milwaukee, Wisconsin) and used without further purification.

**Electrospinning.** A solution containing 10 wt.% TNBT and 10 wt.% PVP in IPA/DMF (volume ratio of 1/1) with trace amount of HAc was first prepared at room temperature as the spin dope for making as-electrospun TNBT/PVP precursor nanofibers. HAc was added in the spin dope to control the hydrolysis/gelation of TNBT. The solution was then filled in a 30 ml BD Luer-Lok™ tip plastic syringe having an 18 gauge stainless-steel needle with 90° blunt end. The electrospinning setup included a high voltage power supply (model number: ES30P), purchased from the Gamma High Voltage Research, Inc., and a laboratory-produced roller with a diameter of 10 inches. During electrospinning, a positive high voltage of 15 kV was applied to the needle; and the feed rate of 1.0 ml/hr was maintained using a digitally controlled, extremely accurate, positive displacement syringe pump (model number: KDS 200) purchased from the KD Scientific Inc. TNBT/PVP precursor nanofibers were collected on the electrically grounded aluminum foil that covered the surface of the roller. The distance between the tip of the needle and the edge of the roller was set at 8 inches, and the rotational speed of the roller was set at 100 rpm. The as-electrospun TNBT/PVP precursor nanofibers was kept under ambient condition of ~20 °C temperature and ~50% relative humidity for a week to allow the TNBT in the nanofibers to completely hydrolyze and turn into a three dimensional network (gel).

**Pyrolysis.** The precursor nanofibers were carefully peeled off from the aluminum foil, transferred into a ceramic boat, and placed in a Lindberg 54453 Heavy Duty Tube Furnace purchased from the TPS Co. for pyrolysis into the final TiO<sub>2</sub> nanofibers. The procedure for pyrolysis included (1) increasing the temperature at the 10 °C per minute rate from the room temperature to 500 °C, (2) maintaining the temperature at 500 °C for 6 hrs to completely burn/remove the organic components in the nanofibers and to allow TiO<sub>2</sub> to crystallize, and (3) naturally cooling off to the room temperature. A constant flow of air was maintained through the furnace during the pyrolysis.

**Characterization of nanofibers.** A Zeiss Supra 40VP field-emission scanning electron microscopy (SEM) and a Rigaku Ultima Plus X-ray diffraction (XRD) at the South Dakota School of Mines and Technology, as well as a Hitachi HF-3300 transmission electron microscopy/scanning transmission electron microscopy (TEM/STEM) at the Oak Ridge National Laboratory, were employed to characterize the morphological and structural properties of both the as-electrospun precursor nanofibers and the resulting final TiO<sub>2</sub> nanofibers. Prior to SEM examination, the specimens were sputter-coated with gold to avoid charge accumulations. A rotating X-ray generator (40 kW, 40 mA) with CuK $\alpha$  radiation (wavelength  $\lambda$  = 1.54Å) was used in the XRD experiments. The XRD profiles were recorded from 20° to 60° at the scanning speed of 2° min<sup>-1</sup>. For the high-resolution TEM characterizations, an acceleration voltage of 100 kV was selected for the precursor nanofibers and an acceleration voltage of 300 kV was selected for the final TiO<sub>2</sub> nanofibers. The TEM specimens were prepared by dispersing fibers onto lacey carbon films supported on 200-mesh copper grids.

Figure S1 is the XRD pattern of the electrospun TiO<sub>2</sub> nanofibers, and Figure S2 is a high resolution TEM image of an individual TiO<sub>2</sub> nanofiber at a broken end. The consistent results from TEM and XRD confirmed that all electrospun TiO<sub>2</sub> nanofibers consisted of anatase-phase TiO<sub>2</sub> crystallites with sizes of approximately 10 nm.

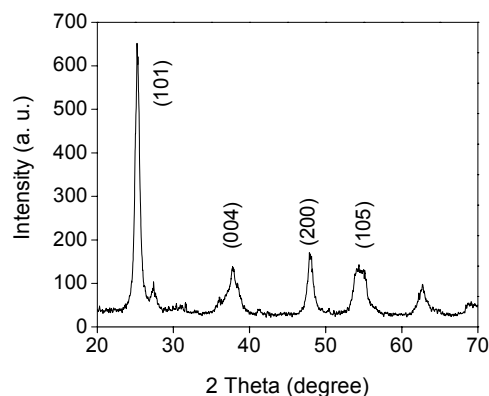


Figure S1. X-ray diffraction pattern of the electrospun TiO<sub>2</sub> nanofibers.

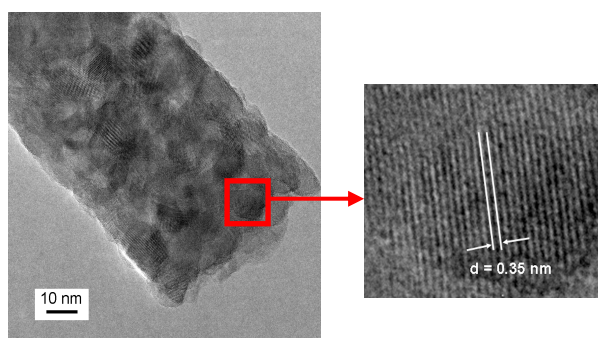


Figure S2. A high resolution TEM image of an electrospun TiO<sub>2</sub> nanofiber.

Figure S3 shows the top-view SEM images of the samples containing 0%, 15%, 50%, and 100% nanofibers by weight. Unlike the original electrospun TiO<sub>2</sub> nanofibers with very large aspect ratio as shown in Figure 2(a), the nanofibers in Figure S3 were broken into shorter ones with lengths ranging from sub-microns to microns due to sonication during the preparation of nanofiber/nanoparticle composites. An SEM image and a schematic representation of an electrospun TiO<sub>2</sub> nanofiber embedded in conventional TiO<sub>2</sub> nanoparticles are shown in Figure S4a and S4b, respectively. Additionally, it was found that as the nanofiber percentage increases, more nanofibers aggregated together, resulting in reduced dye attachment (uptake).

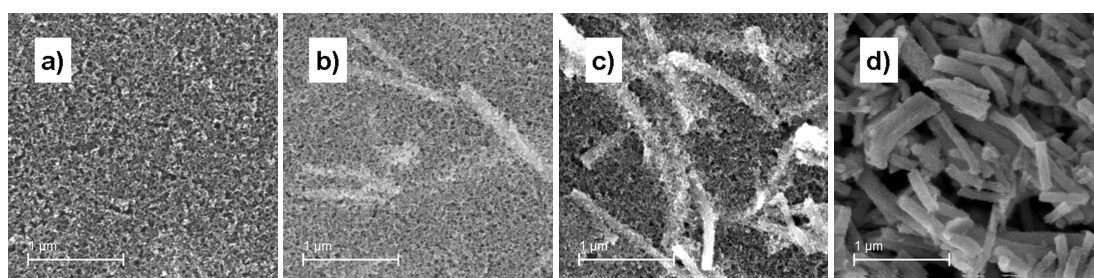


Figure S3. Top-view SEM images of the samples with the nanofiber weight percentages being (a) 0%; (b) 15%; (c) 50%; and (d) 100%.

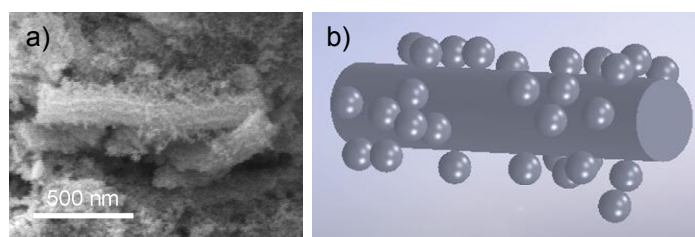


Figure S4. (a) An SEM image and (b) a schematic representation of an electrospun TiO<sub>2</sub> nanofiber embedded in conventional TiO<sub>2</sub> nanoparticles.

## 2. Dye desorption experiment

To measure the amount of attached dye onto composite film (photoanode), the dye on the TiO<sub>2</sub> nanofiber/nanoparticle composite was desorbed into a mixture solution of 0.1 M NaOH and ethanol at 1:1 ratio by volume. The concentrations of the desorbed dye were then measured using UV-Vis absorption spectroscopy and calculated using Beer–Lambert Law as below:

$$c = \frac{A}{\varepsilon \cdot l} \quad (2)$$

where  $A$  is the absorbance,  $\varepsilon$  is the extinction coefficient, and  $l$  is the path-length of the sample.

The mole amount of the desorbed dye was then calculated:

$$M = c \cdot V \quad (3)$$

where  $V$  is the volume of the NaOH and ethanol mixture solution. The mole amount per gram of TiO<sub>2</sub> is calculated as:

$$t = \frac{M}{m} \quad (4)$$

where  $m$  is the mass of TiO<sub>2</sub> nanofiber/nanoparticle composite. By combining the above equations, the mole amount of dye per gram of TiO<sub>2</sub> nanofiber/nanoparticle composite was obtained:

$$t = \frac{A \cdot V}{\varepsilon \cdot l \cdot m} \quad (5)$$

To determine the extinction coefficient ( $\varepsilon$ ), the absorbance at varied known concentrations of dye in the solution of NaOH and ethanol was measured. The extinction coefficient,  $\varepsilon$ , was calculated to be 11.82 mM<sup>-1</sup>cm<sup>-1</sup> for N719 at the wavelength of 512 nm using Beer–Lambert Law.

With the above method, the TiO<sub>2</sub> nanofiber/nanoparticle samples with nanofiber weight percentages of 0%, 15%, 50%, and 100% were prepared and their corresponding masses were measured.

## 3. Fabrication and testing of DSSCs

A paste containing TiO<sub>2</sub> nanoparticles with the average size of ~9 nm (Ti-Nanoxide HT) was purchased from Solaronix. The specific surface area of the nano-porous TiO<sub>2</sub> film was ~160 m<sup>2</sup>/g. To prepare TiO<sub>2</sub> nanofiber/nanoparticle composites, the nanofibers were first dispersed in anhydrous ethanol followed by sonication; the paste was subsequently added, and finally the mixture was sonicated again to disperse the nanofibers uniformly in the nanoparticle matrix. The samples with 0%, 15%, 50%, and 100% nanofibers by weight were prepared respectively.

The fluorine-doped tin dioxide (FTO) glass substrates with a sheet resistance of ~8 Ω/□ and a transparent conducting layer thickness of ~400 nm were cleaned using a sonicator in a detergent solution, de-ionized water, acetone, and isopropanol for 15 min each in succession, and then treated with oxygen plasma for 10 min.

The photoanodes were prepared by applying the nanofiber/nanoparticle composites onto the FTO substrate, which was pre-coated with a thin compact layer of 0.2 mM titanium di-isopropoxide bis (acetylacetonate), by doctor blading. The thicknesses of the films were controlled by varying the tape thickness and composite viscosity. The photoanodes were sintered at 100°C for 30 minutes and then 450 °C for 45 minutes. The TiO<sub>2</sub> composites were then treated with TiCl<sub>4</sub> and sintered again as above. The photoanodes were then soaked in a 0.5 mM solution of N719 dyes in a mixed solution of acetonitrile and tert-butyl alcohol with 1:1 volume ratio at room temperature for 48 hours. The counter electrodes were prepared by sputtering platinum onto the FTO glass substrates. The electrodes were sealed using parafilm. The electrolyte was a redox couples I<sup>-</sup>/I<sub>3</sub><sup>-</sup> containing 0.60 M BMII, 0.03 M I<sub>2</sub>, 0.10 M GuSCN, 0.5 M tert-butylpyridin in a mixture solvent of acetonitrile and valeronitrile (85:15 volume ratio). The DSSCs were tested for current-voltage characteristics under the illumination of a solar simulator with light intensity of 100 mW/cm<sup>2</sup>, and for incident photon to current conversion efficiency (IPCE) under a calibrated monochromator. The cell efficiencies were further confirmed using the Hamamatsu reference cell calibrated by the National Renewable Energy Laboratory.