

## Electronic Supplementary Information (ESI)

### **TiO<sub>2</sub> nanoparticles @ TiO<sub>2</sub> nanofibers-an innovative one-dimensional material for dye-sensitized solar cells**

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# ESI 1

## Experimental methods

### **Materials**

Titanium isopropoxide (TiP, 99.99%, Aldrich, Germany), acetic acid (99.9%, Alfa Aesar, USA), isopropyl alcohol (absolute, Alfa Aesar, USA), methanol (absolute, Aldrich, Germany), triton-X-100 (molecular biology grade, Aldrich, Germany), polyvinyl pyrrolidone (PVP,  $1.3 \times 10^6$ , M.P  $> 300$  °C, Aldrich, Germany), acetonitrile (99.9%, Aldrich, USA), tertiary butyl alcohol (99.9%, Aldrich, USA), and N719 dye (cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis (tetrabutylammonium)) from Solaronix Switzerland) were used as received. Fluorine-doped tin oxide (FTO, size  $2 \times 2$  cm<sup>2</sup>, sheet resistance of  $\sim 8 \Omega \square^{-1}$  was made in-house using a spray-pyrolysis deposition unit starting from Corning Glass (Eagle XG, USA).

### **Preparation of TiO<sub>2</sub> colloidal solution for electrospaying**

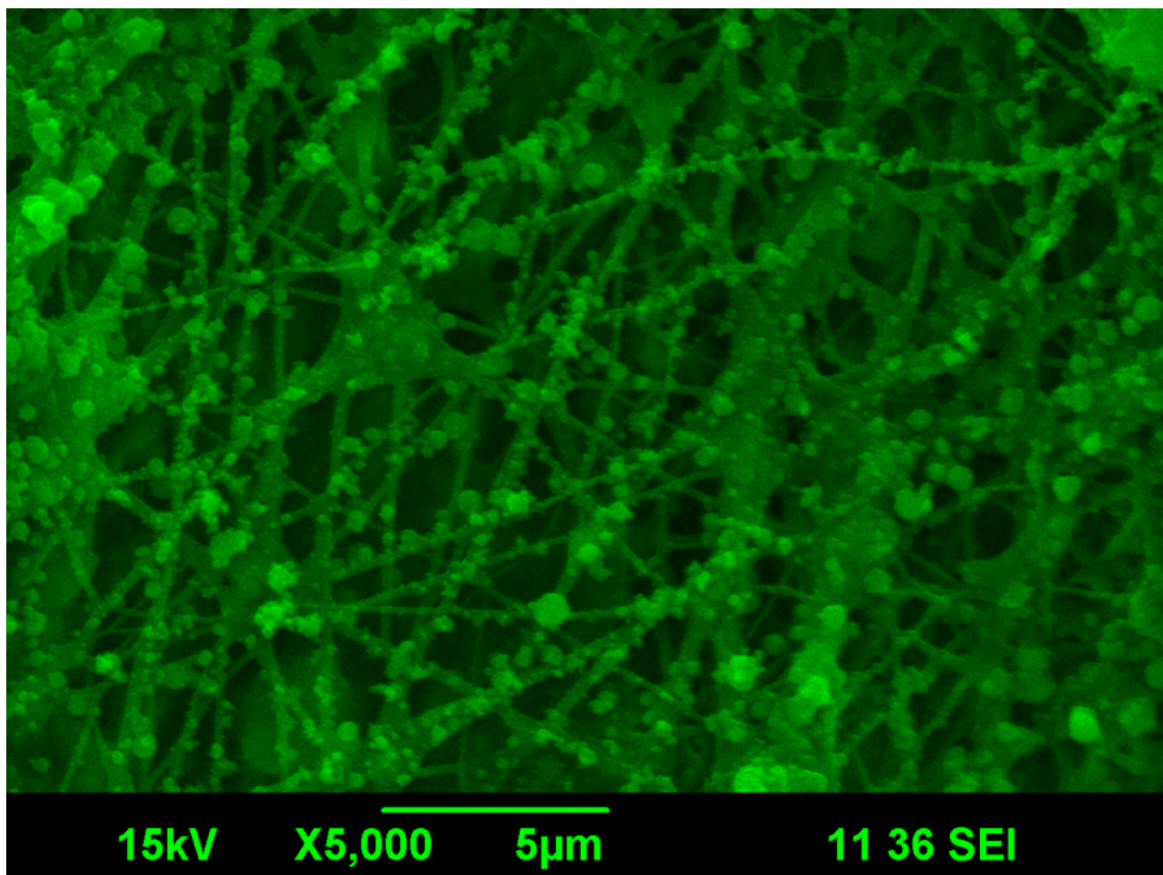
The colloidal solution containing TiO<sub>2</sub> nanoparticles for electrospaying was prepared using the following protocol.<sup>1</sup> 20 mL TiP and 2.5 mL glacial acetic acid were added to 25 mL isopropyl alcohol. This solution was subjected to continuous steam supply (till the total volume of the solution became 25-30 mL). This results in rapid hydrolysis of TiP resulting in the formation of a thick TiO<sub>2</sub> colloid. This thick colloid was ground with 50 mL water using a mortar and pestle and subsequently autoclaved at 180 °C for 3 h. 20 mL of the autoclaved solution was added to a mixture of 2.5 mL acetic acid, 10 mL isopropyl alcohol and 5 drops of triton-X-100 and sonicated thoroughly for 1 h before electrospaying.

### **Preparation of the polymeric solution of TiO<sub>2</sub> for electrospinning**

About 6 wt. % polyvinyl pyrrolidone (PVP) solution was made in 10 mL of methanol. To this 3 mL of glacial acetic acid was added and stirred well followed by the addition of 2 mL of TiP.<sup>2</sup> The prepared solution was stirred for 2 h before electrospinning.

## Preparation of fiber- particle composite by simultaneous electrospinning and electrospaying

For the electrospinning process, the prepared solution was taken in a 10 mL syringe and fed to the electrospinning set-up (Zeonics, India). Fibers were spun at a voltage of 13 kV with a tip-to-target distance 10 cm and at a flow rate 1.2 mL/h. The TiO<sub>2</sub> colloidal solution for electrospaying was also fed to a 10 mL syringe to another pump vertically opposite to that of electrospinning (see the schematic in Fig. 1 for the arrangement). The stable colloidal system was sprayed at a voltage of 8 kV with a flow rate of 1 mL/ h. The needle-to-collector distance was kept at 8 cm. The electrospun fibers containing the electrospayed particles were collected on a grounded aluminium (Al) foil wrapped on the rotating drum which was rotating with an angular velocity of 3000 rpm. The fiber-particle composite was deposited in the form of a thick white sheet which was peeled-off from the Al foil and kept for annealing (in air medium) at 450 °C for 3 h for the degradation of polymer and get crystallized TiO<sub>2</sub>. Figure below shows an SEM image of the fiber-particle composite.



## **Characterization of the nanocomposite**

The crystal structure analysis of the fiber-particle composite was carried out using X-ray powder diffractometer (X'Pert PRO Analytical) with Cu K $\alpha$  radiation (with a current of 30 mA, voltage of 40 kV and data interval of 0.03°). The phase identification was done using the standard JCPDS database. The Raman spectrum was acquired using a Confocal Raman Spectrometer (WITEC ALPHA 300 RA). X-ray photoelectron spectroscopy (XPS, Kratos Analytical, Ultra Axis) was also done for the purity analysis under standard protocol. The morphological analysis was carried out using a Scanning Electron Microscopy (SEM) (JEOL JSM 6490 LA) and Transmission Electron Microscopy (TEM) (SEI Tecnai G2 30). About 5 mg of the sample was dispersed in 10 mL methanol under sonication. A drop of the solution was cast on a carbon-coated copper grid and allowed to dry first under ambient conditions and then in vacuum. This was used for TEM analysis. The absorbance measurements were done using a UV-Vis spectrophotometer (Shimadzu UV-3600). Photovoltaic characterization was performed under 1 Sun simulated sunlight (Newport, Oriel class A) under AM1.5G conditions. *I-V* curves were recorded with a Keithley 2400 digital source meter under an applied external potential scan for an exposed area of 0.20 cm<sup>2</sup> (using masking). IPCE characterization was done using an Oriel Newport (tracq basic, model 77890) configured for dye-sensitized solar cells.

## **Fabrication of Dye-sensitized Solar Cells**

### **a. Synthesis of liquid polymer**

The liquid polymer used for the TiO<sub>2</sub> paste preparation (for screen printing) was synthesized using an already reported procedure.<sup>2</sup> Ethylene glycol (8.15 g) was taken in an RB flask and heated to 80 °C in an oil bath. At 80 °C, 1.42 g of TiP was added and stirred well. Once titanium isopropoxide was completely dissolved, 6.3 g of citric acid was added and temperature was raised to 100 °C. The mixture was kept at the same temperature under slow stirring for about 5 h. The resulting clear polyester was kept overnight for cooling down to room temperature.

### **b. Doctor-blading process**

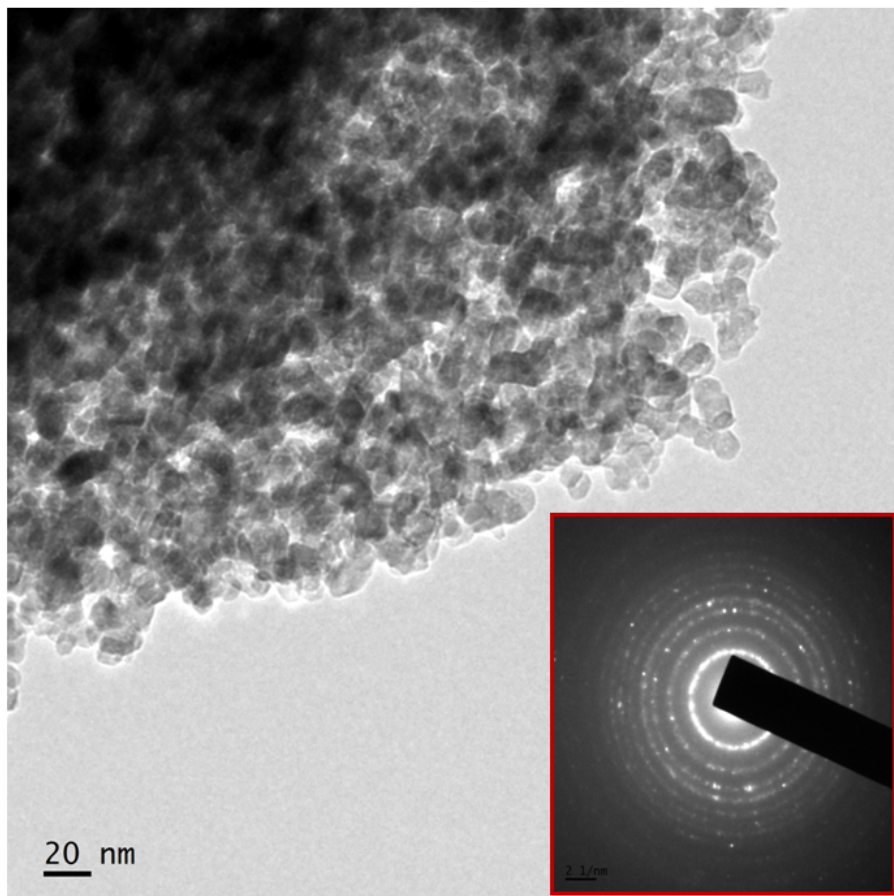
200 mg of the prepared fiber-particle composite was mixed with 250  $\mu$ L of the polyester. The composite was kept under sonication for 24 h to get slurry of right rheology necessary for doctor-

blading. This paste was doctor-bladed on an FTO plate which was pre-coated with a thin layer of TiO<sub>2</sub> colloid (100 nm thick) using spray pyrolysis deposition (SPD). Being a new material architecture, we wanted to know the optimum thickness needed for best performing cells and therefore the DSC study was performed in a thickness dependent manner. Control experiments were done under similar conditions using the TiO<sub>2</sub> fibers and nanoparticles, separately.

### **c. Fabrication of DSC**

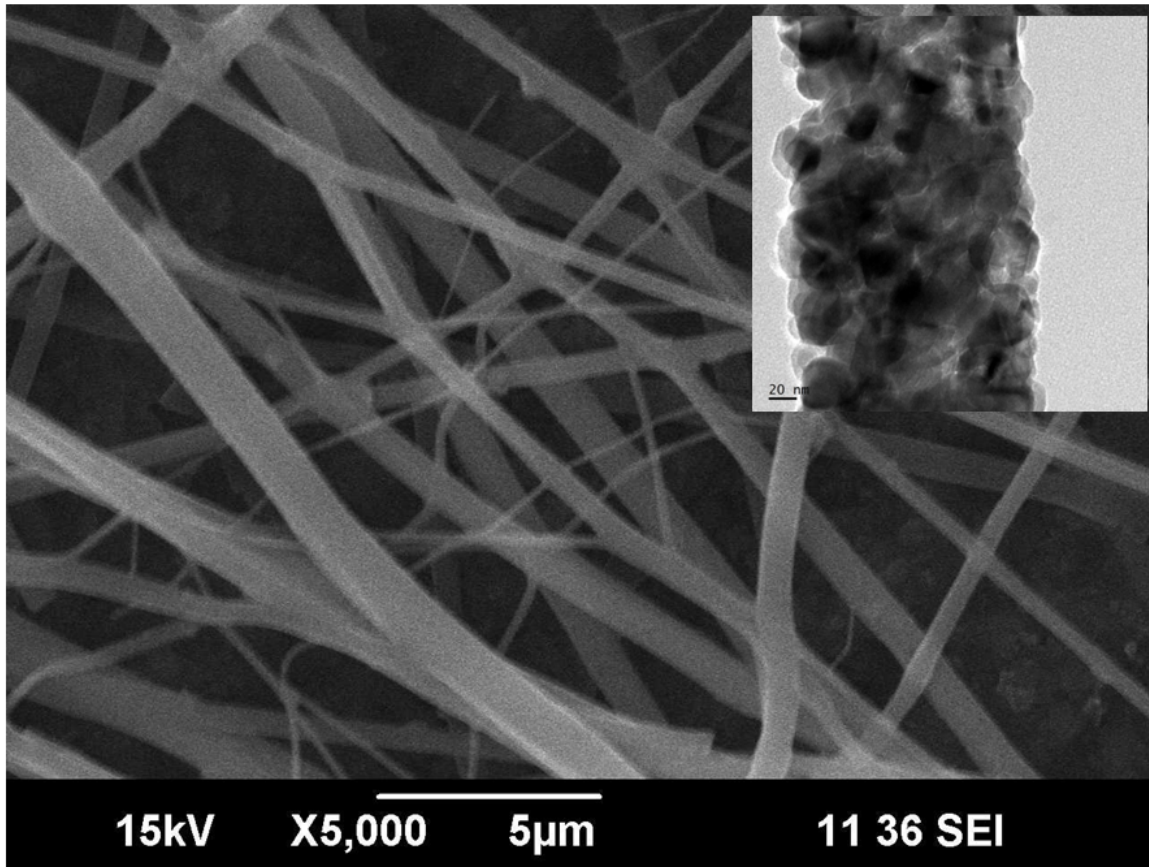
The doctor-bladed FTO plates were kept in the oven at 80 °C for drying. The dried samples were kept in the furnace for annealing at a temperature of 450 °C for 3 h. The square-shaped electrodes had thicknesses of 11, 14, 18 and 20 μm, respectively, with an exposed area of 0.2 cm<sup>2</sup>. After annealing, the samples were treated with 30 mM TiCl<sub>4</sub> for half an hour. The treated electrodes were again annealed at 450 °C for another 3 h before cooling down to 120 °C for dye-sensitization. The dye solution (0.5 mM N719 dye) was prepared in 1:1 acetonitrile-tert butyl alcohol mixture. Dye sensitization was accomplished by immersing the annealed electrodes in the dye solution for 24 h without getting exposed to moisture. After 24 h, the sensitized electrodes were taken out and washed repeatedly with methanol to remove the unanchored dyes. The solar cell was assembled by placing a platinum coated counter electrode (hole-drilled) on the sensitized electrode in presence of a spacer. The I<sub>3</sub><sup>-</sup>/I<sup>-</sup> electrolyte was filled using vacuum backfilling process. After testing, the electrodes were dismantled, the photoanode was washed with methanol (to remove the electrolyte) and dipped in 0.1 M NaOH solution for dye desorption. The desorbed dye was quantified using UV-Vis measurements.

## ESI 2



A TEM image of the TiO<sub>2</sub> nanoparticles used for the control experiment. The particles have an average diameter of about 15 nm. Inset shows the polycrystalline nature of the particles.

## ESI 3



SEM image of the electrospun TiO<sub>2</sub> nanofibers used for the DSC control experiment. Inset shows the TEM image of a single nanofiber showing that the nanofibers are made up of small spherical particles of ~ 20 nm sizes.

### References

1. G.R.A. Kumara, S. Kawasaki, P.V.V. Jayaweera, E.V.A. Premalal, and S. Kaneko, *Thin Solid Films*, 2012, **520**, 4119-4121.
2. A. S. Nair, R. Jose, Y. Shengyuan, and S. Ramakrishna, *J. Colloid Interface Sci.*, 2011, **353**, 39-45.