# Electronic Supplementary Information (ESI)

# Ultrafine $TiO_2$ Nanofibers for Photocatalysis

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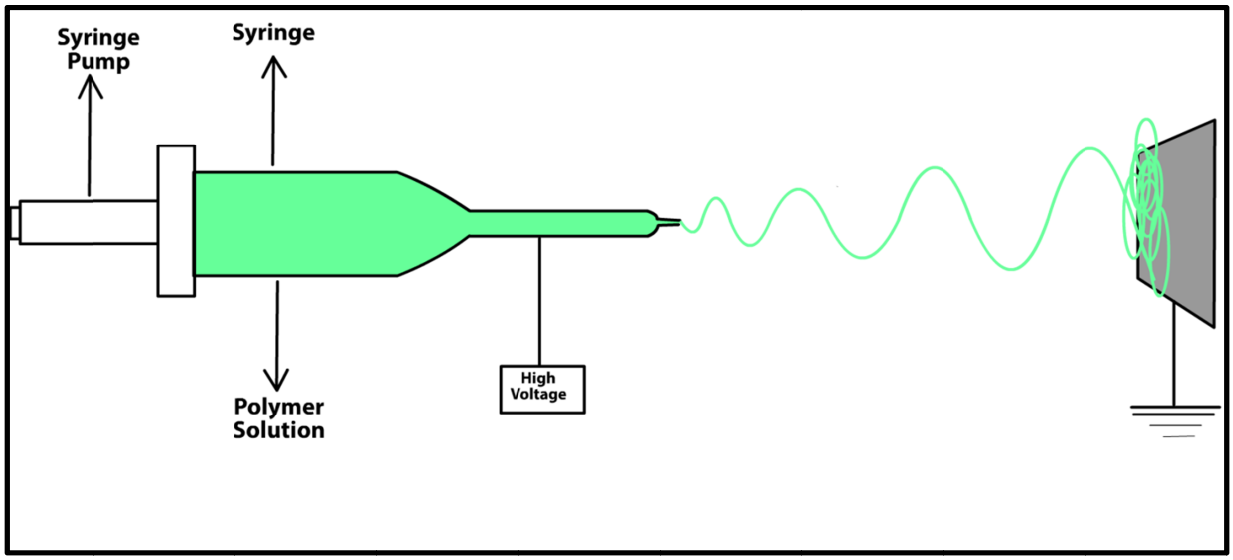
## ESI 1




## ESI 2

**Materials and Methods**

### (a) Materials

Titanium (IV) isopropoxide (TiP,99.99%,Aldrich,USA), polyvinyl acetate (PVAc, Mw 500,000, Sigma Aldrich, USA), glacial acetic acid (Nice Chemicals, India), N749 dye (Dyesol, Australia, Mw-1364.98), *N,N*-dimethyl acetamide (DMAc, Nice Chemicals India), KOH pellets (Merck Germany) and HCl (Nice Chemicals, India) were used as received. For making aq. solutions of the materials, Millipore water was used.

### (b) Fabrication of electrospun rice-shaped $TiO_2$

The rice grain-shaped $TiO_2$ mesostructures were fabricated by electrospinning. The $TiO_2$ sol was

prepared by the following route: 1.2 g of polyvinylacetate was added to 10 mL of *N,N*-dimethyl acetamide (DMAc) under magnetic stirring. When the PVAc was dissolved in the solvent properly, 2 mL of acetic acid and 1 mL of TiP were added. The mixture was stirred at room temperature for 12 h to obtain a uniform blend. Electrospinning was done using a commercial machine (Zeonics System, India). The voltage applied was 16 kV and the distance between the needle (21G 1½) tip and the rotating collector (which was wrapped with Al foil) was ~ 10 cm. The flow rate was maintained at 1mL/h. The humidity level of the electrospinning chamber was kept at ~55%. After electrospinning, the $TiO_2$-PVAc composite nanofibers were peeled-off from the Al foil and sintered at $450^0$C for 3 h with a ramping rate of $2^0$C/min to sublimate the PVAc from the composite. During the sintering process, the continuous fibers breakdown into finely distributed porous rice-shaped $TiO_2$.The reasons for such a structural transformation had already been accounted by us in previous papers.

**(c) Fabrication of ultrafine nanofibers from the rice-shaped $TiO_2$**

Six hundred milligrams of the rice grain shaped $TiO_2$ was subjected to a hydrothermal treatment with 60 mL of 5M KOH solution in a steel hydrothermal bomb, lined with a Teflon coating at 180°C for 24h. The entire setup was then cooled to room temperature. The treated materials (the potassium titanates) were washed repeatedly with de-ionised water and subsequently soaked in 0.1 M HCl at room temperature for 24 h. The acid-treated material was collected and washed several times with water and sintered at 180 $^0$C for 30 min. These treated samples were used for subsequent analysis by spectroscopy, microscopy and BET surface area measurements.

**(d) Photocatalytic application**

For this experiment, a stock solution of 2 mg methyl orange (MO) in 250 mL water was prepared. To study the degradation of MO on thin films, the ultrafine $TiO_2$ nanofibers and the commercial P-25 were doctor-bladed on plain glass plates on an area of 2.5 $cm^2$ by doctor-blading technique. Doctor-blading was done by mixing 100 mg of the respective $TiO_2$ with 100 $\mu$L of polyester (as explained in ref. 14c in manuscript)) and spreading the slurry on glass plates. Upon sintering the films at 450 $^0$C for 3 h, the polymer degrades from the film leaving highly porous $TiO_2$ films on glass. A drop of the MO dye was put on the respective films and was UV irradiated (dynamic UV light source, Sankyo Denki, Japan, 15W) for 20 min. Digital

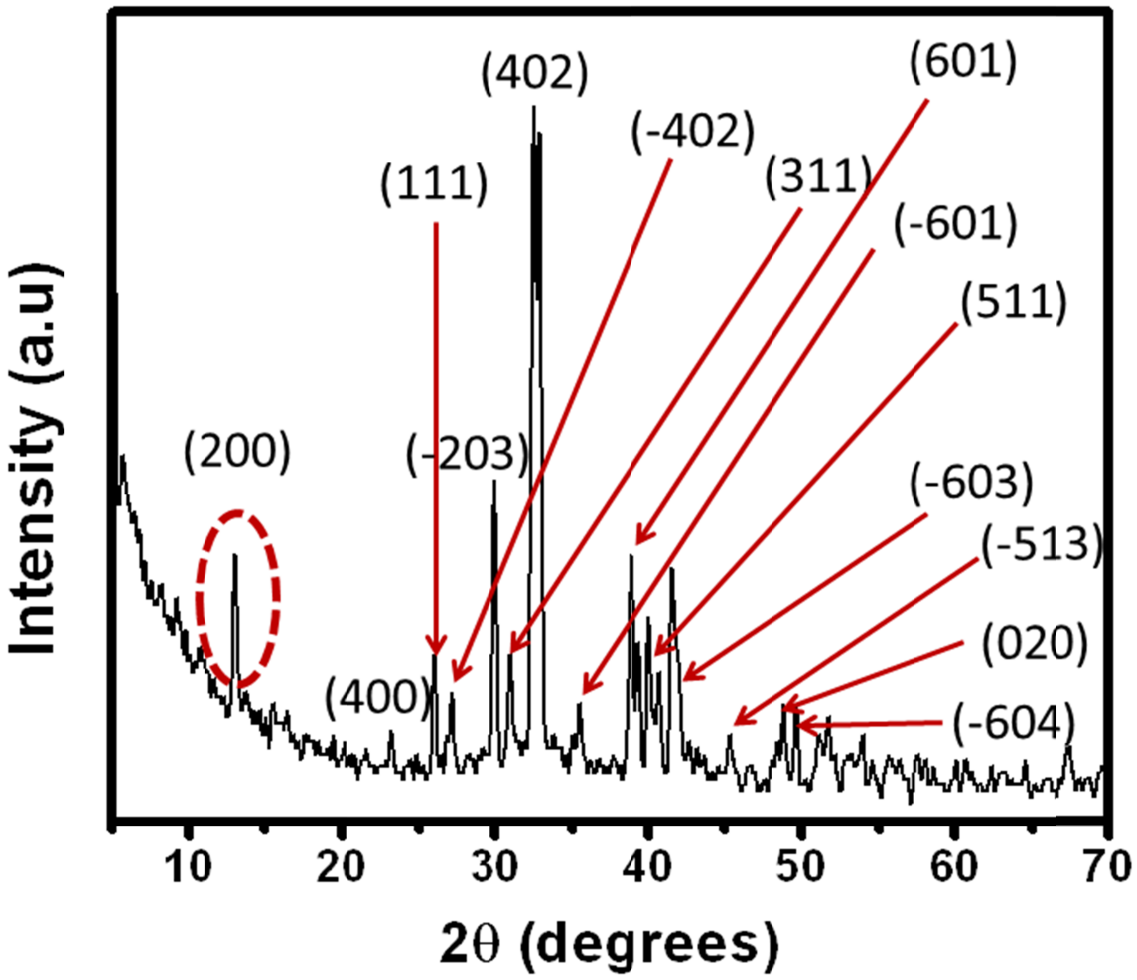
photographs of the films were recorded at every 5 min interval.

## ESI 3

### Characterization

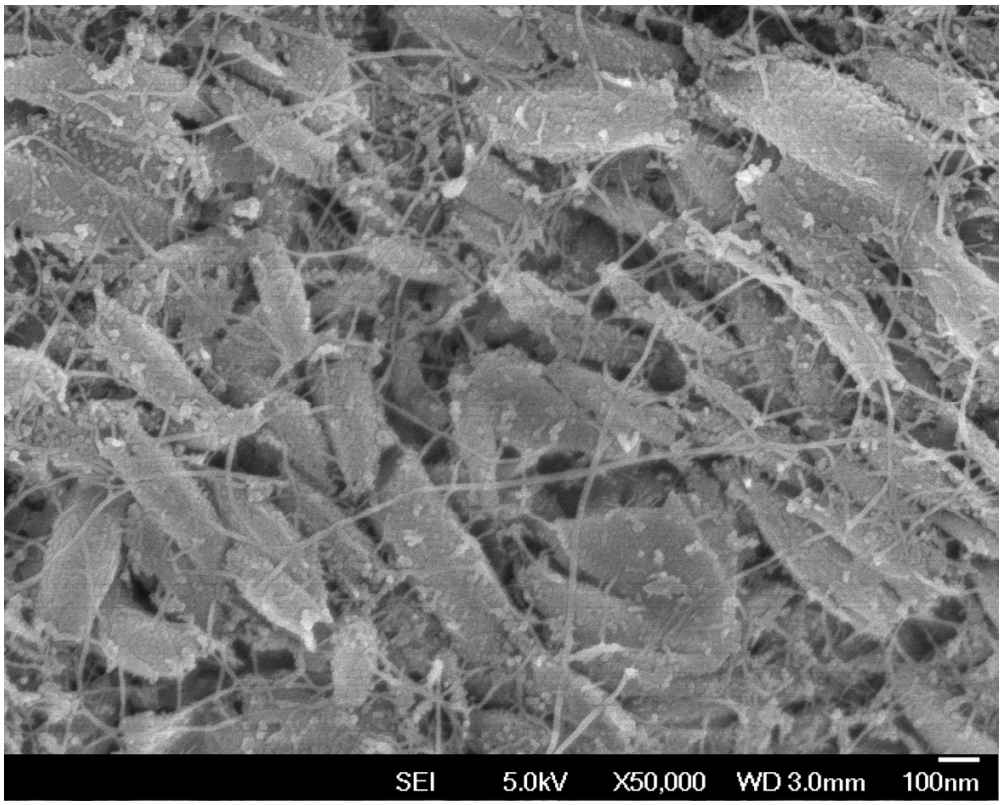
Morphological and structural analyses for the processed nanofibers were done using scanning electron microscopy (JSM 6490 LA, JEOL, Tokyo, Japan). The high-resolution transmission electron microscopy (HR-TEM) was performed using a JEOL 3010 machine operating at 300 kV. Samples for HR-TEM were prepared by dispersing the respective TiO2 in methanol under sonication and then allowing a drop of this suspension to dry on a carbon-coated copper grid. BET measurements were performed using Micromeritics analysis software (TriStar II 3020 V1.03 (V1.03)) at 77K to determine the surface area and pore size and pore volume distributions. Prior to BET measurements, the treated samples were dried under flowing $N_2$ at 350 °C overnight at 77 K. Phase analyses were done using Powder XRD (X'Pert PRO Analytical) spectrometer. X-ray photoelectronspectroscopy (XPS) was done using Kratos Analytical, Ultra axis machine(calibrated) under standard protocols (Monochromatic Al Kα X-ray (hν = 1486.6 eV, incident angle of 300 with respect to surface normal, collection of photoelectrons at a take-off angle of 500 with respect to surface normal, analysis area of ~ 400 nm in diameter and analysis depth of ~ 10 nm). The carbon correction was done using manufacturer's standard software. The optical properties were determined by UV-Vis spectroscopy (Shimadzu UV-3600UV-VIS-NIR spectrophotometer). Raman spectrum of the $TiO_2$ was measured using a calibrated Witec alpha300 R confocal Raman microscope using an excitation laser of 488 nm (wavelength) and power of 0.6 μW. The spot-size was > 2 μm. Atomic absorption spectra (AAS) of the potassium titanate (washed with methanol and water, respectively) were measured using a Perkin Elmer Atomic Absorption Spectrometer, USA (AAnalyst 100).

**ESI 4**



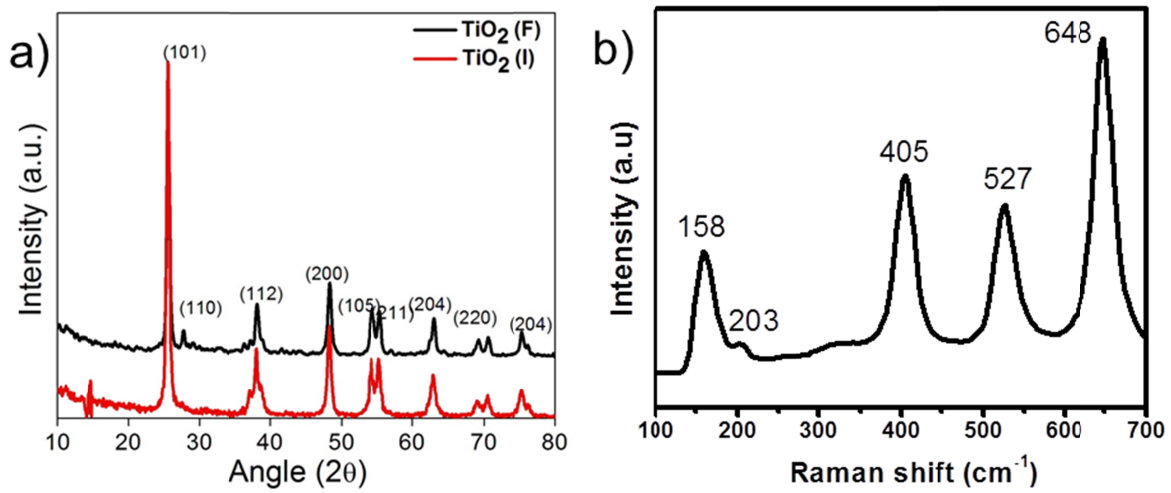

Powder XRD pattern of the $K_2Ti_3O_7$ (JCPDS File No. 40-0403). The peak around 2 θ = 12 is indicative of the structure of titanate. All major peaks are indexible as per the JCPDS file.

**ESI 5**



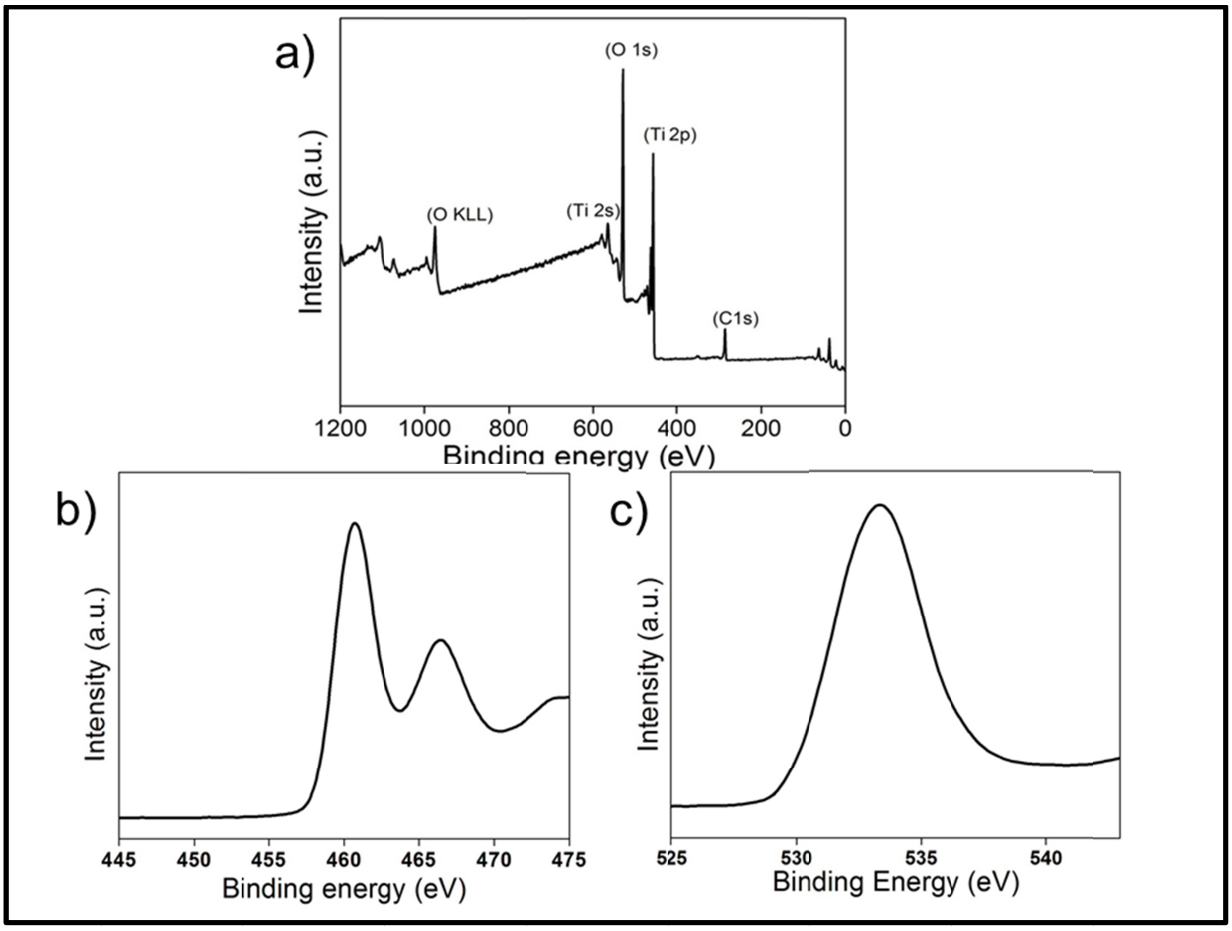

SEM image of the rice-shaped $TiO_2$ during the titanate process (after ~ 5 h) showing the evolution of ultrafine fibers from the mesostructures.

**ESI 6**




a) A comparison of the XRD pattern of rice-shaped $TiO_2$ (red trace) and the ultrafine $TiO_2$ nanofibers (black trace). b) Raman spectrum of the $TiO_2$ nanofibers.

**ESI 7**




Survey spectrum of the $TiO_2$ nanofibers (a) and high-resolution spectra of the Ti and O (b & c, respectively).