Electronic Supplementary Information

Rice grain-shaped TiO_2 mesostructures by Electrospinning for Dye-sensitized Solar Cells

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Supporting Information (SI) 1

Synthesis and characterization of the TiO_2 meso rice grains: Polyvinyl acetate (PVAc, Mw = 500000, Sigma Aldrich, US), polyvinyl pyrrolidone (PVP, 1.3×10^6, M.P > 300^0 C, Aldrich, Germany), titanium tetra (IV) isopropoxide (TIP, 97%, Aldrich, Germany), N, N-dimethyl formamide (DMF, 99.8%, GC grade, Merck, Germany), N,N-dimethyl acetamide (DMAc, 99.8%, GC Grade, Aldrich, Germany), ethanol (absolute, Fischer scientific, Leicestershire, UK), acetic acid (99.7%, LAB-SCAN Analytical Sciences, Thailand), acetonitrile (99.9%, Merck, GC grade) and tertiary butyl alcohol (99%, GC grade, Fluka, Germany) were used as received. N3 dye (*cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium(II)) was purchased from Solaronix, Switzerland and used as received. Fluorine-doped tin oxide (FTO, size = 1.5 × 1.0 cm^2, sheet resistance of 25 Ω/□) plates were from Asahi Glass, Japan.

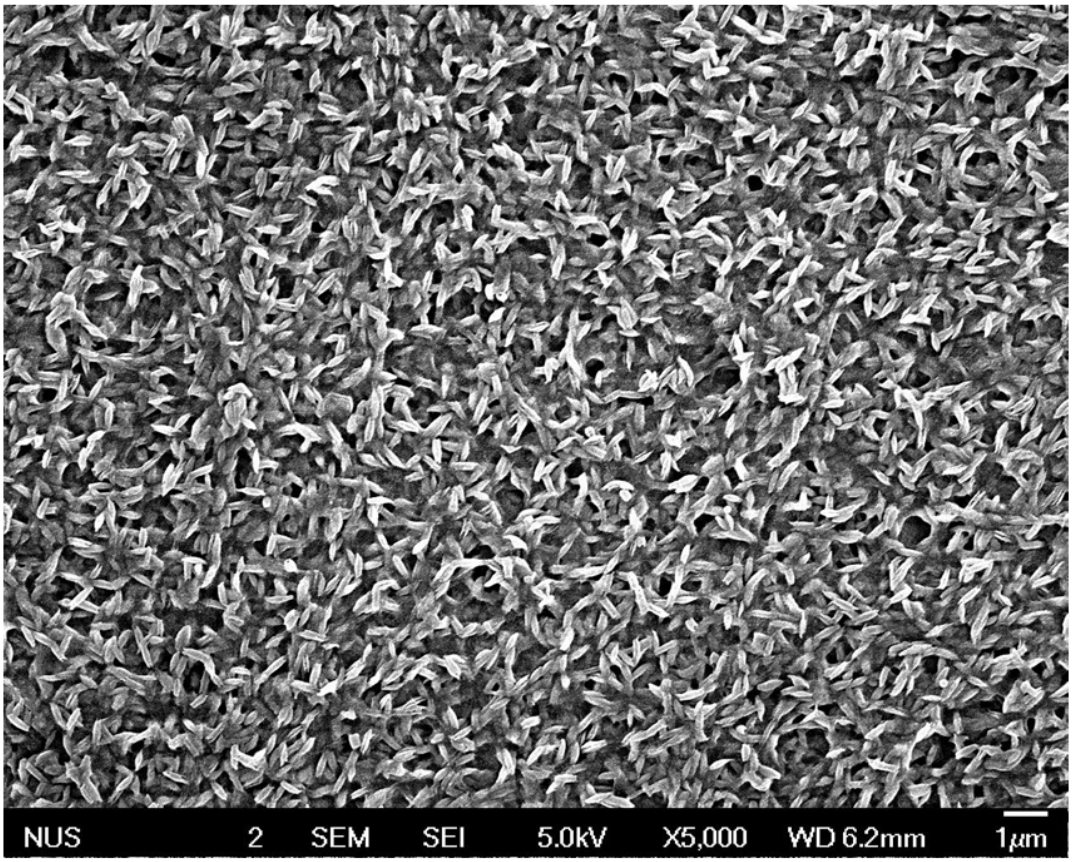
PVAc (1.2 g) was added to 10 mL of DMAc. This was followed by the addition of 2 mL of acetic acid and 1 mL of TIP. The mixture was stirred well for about ~ 12 h before electrospinning (E-spinning). E-spinning was done using a commercial machine, NANON (MECC, Japan) under an applied voltage of 30 kV. The distance between the needle (27G ½) tip and the collector (which is a rotating drum with aluminimum foil wrapped around it) was ~ 10 cm. The humidity level at the E-spinning chamber was between 50-60 %. The as-spun nanofibers and the sintered mesostructures were characterized by scanning electron microscopy (SEM, JEOL JSM-6701F microscope operated at 30 kV fitted with an energy dispersive X-ray spectroscope (EDS) and a Quanta 200 FEG System, FEI Company, USA, operated at 15 kV, respectively), high-resolution transmission electron microscopy (HR-TEM, JEOL 3010 operated at 300 kV), BET surface area (NOVA 4200E Surface Area and Pore Size Analyzer, Quantachrome, USA), powder X-ray diffraction (XRD, Bruker-AXS D8 ADVANCE) and UV-visible (Schimadzu UV-3600 UV-VIS-NIR spectrophotometer) spectroscopy. Photocurrent measurements were carried out using a XES-151 S solar simulator (San-Ei, Japan) under AM1.5 G condition. The level of standard irradiance (1 Sun conditions, 100 mW/cm^2) was set with a calibrated c-Si reference solar cell.

Dye-sensitized solar cells (DSCs) were fabricated by direct spinning of the TiO_2-PVAc composite on cleaned FTO plates. The composite was spun for ~ 3 h (under the conditions mentioned above) and were annealed at 500^0 C for 1 h in air to get rice grain-shaped TiO_2 nanostructures of ~ 12 μm thickness on FTOs. When the temperature reached 80^0 C during the cooling stage, the FTOs were taken out and soaked in 0.5 mM N3 dye solution for about 24 h for saturate chemisorption of the sensitizer on TiO_2 surfaces. These were then gently washed in absolute ethanol for removing excess/surface-adsorbed N3 dyes. DSCs were constructed under standard protocols by sandwiching the dye-anchored TiO_2 against a platinum-sputtered FTO in presence of I_3/I^- electrolyte.

Supporting Information (SI) 2

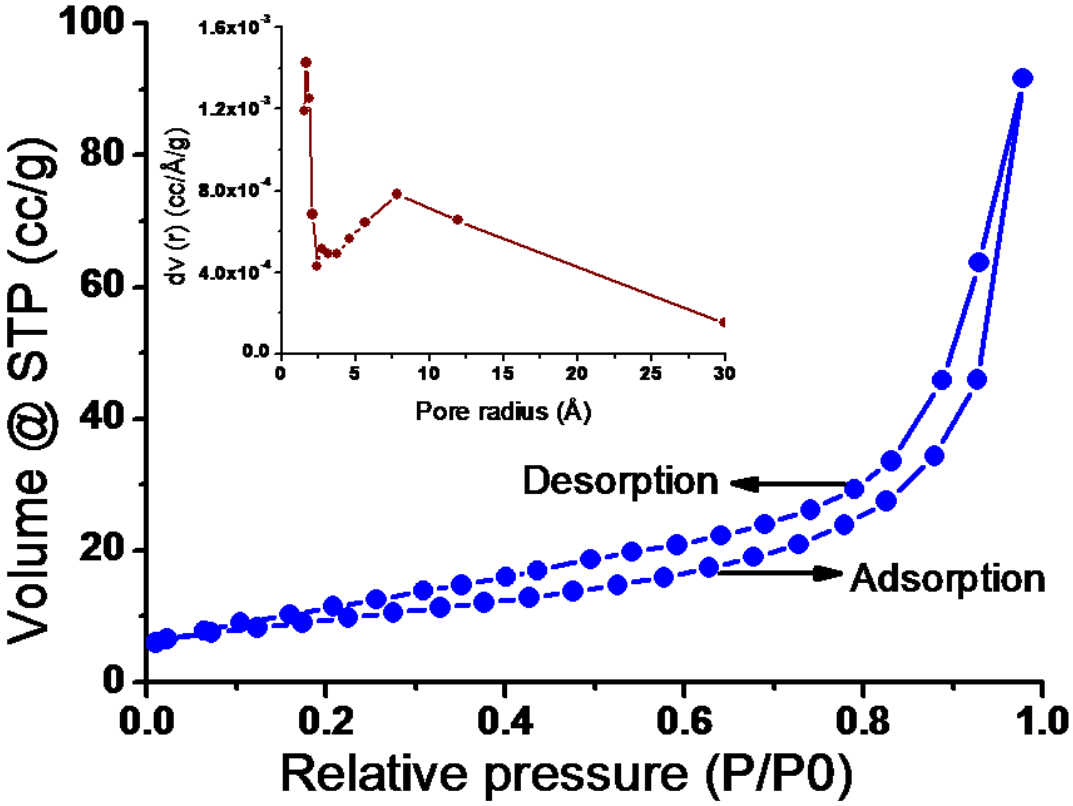
High resolution SEM (HR-SEM) image of the TiO_2 meso rice grains. Each rice grain structure was found to be porous.

Supporting Information (SI) 3



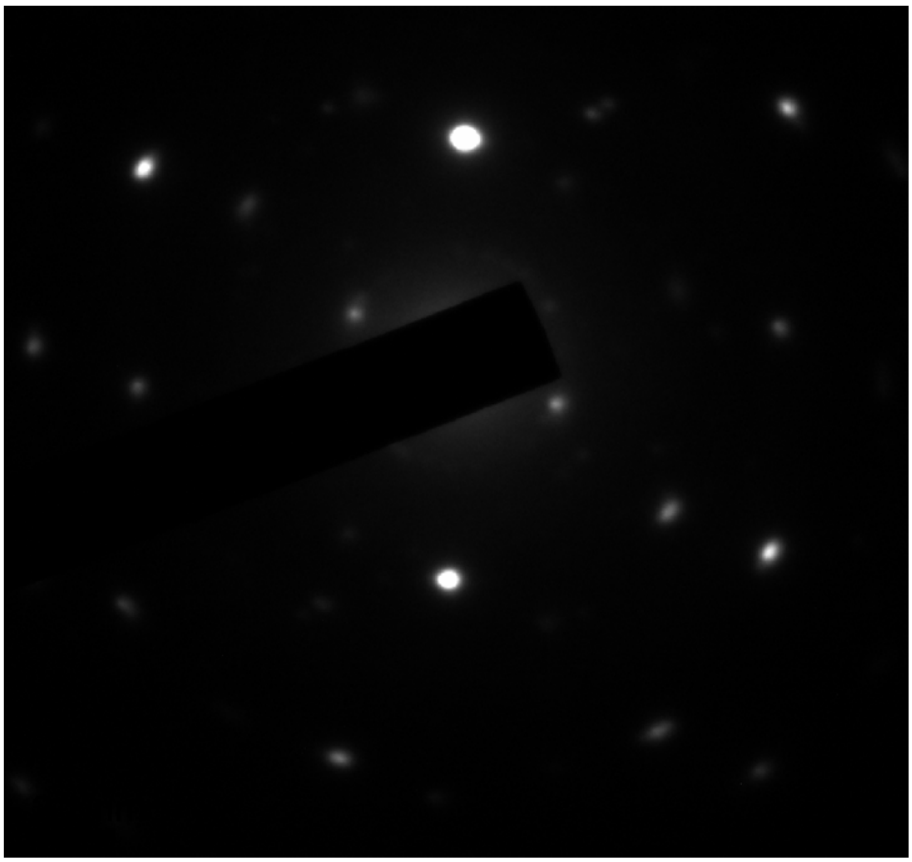
SEM image of the rice-grain shaped TiO_2 obtained by sintering the PVAc-TiO_2 composite nanofibers at 450^0 C for 1 h.

Supporting Information (SI) 4



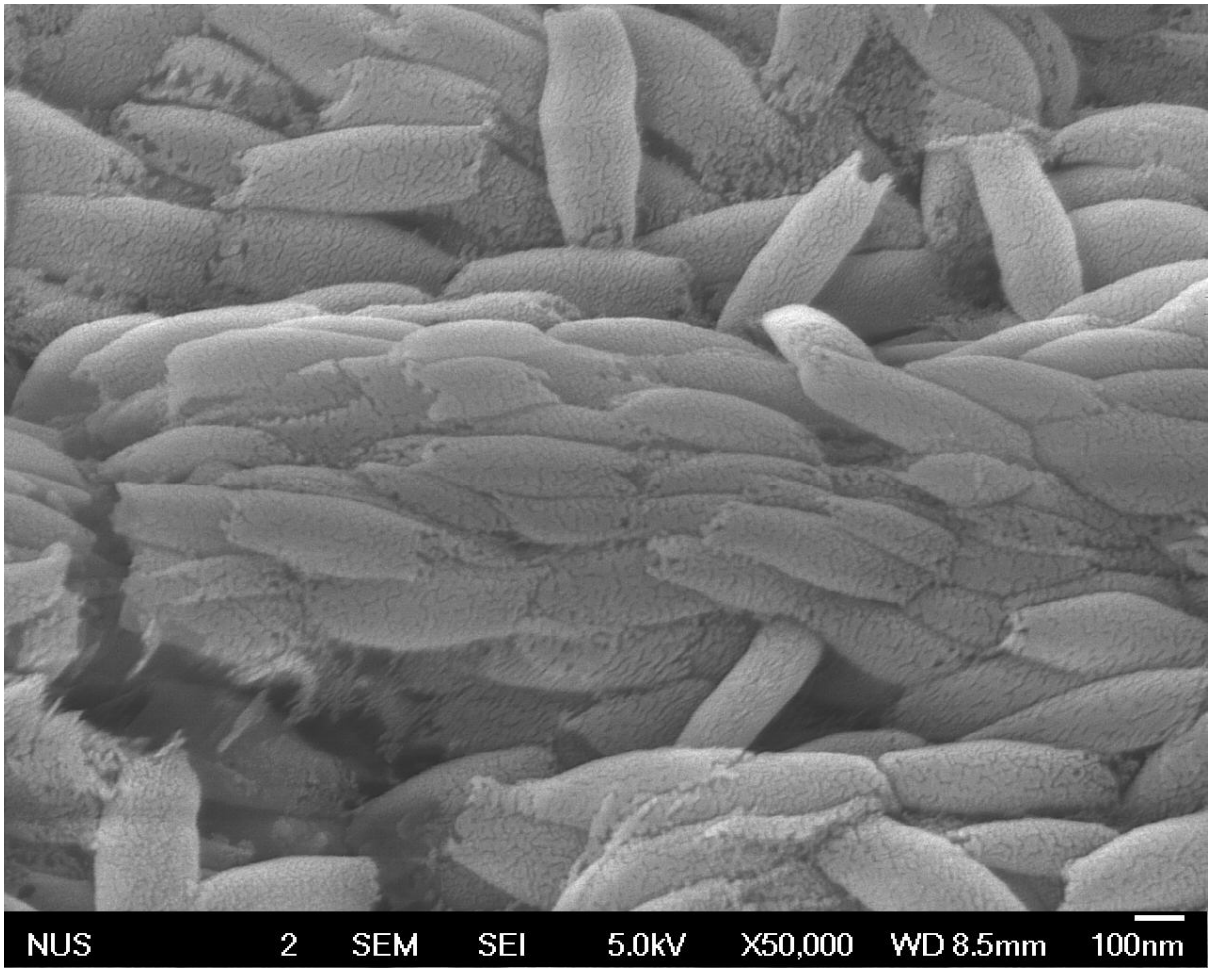
BET isotherm of the TiO_2 meso rice grains. Inset shows the pore size distribution.

Supporting Information (SI) 5



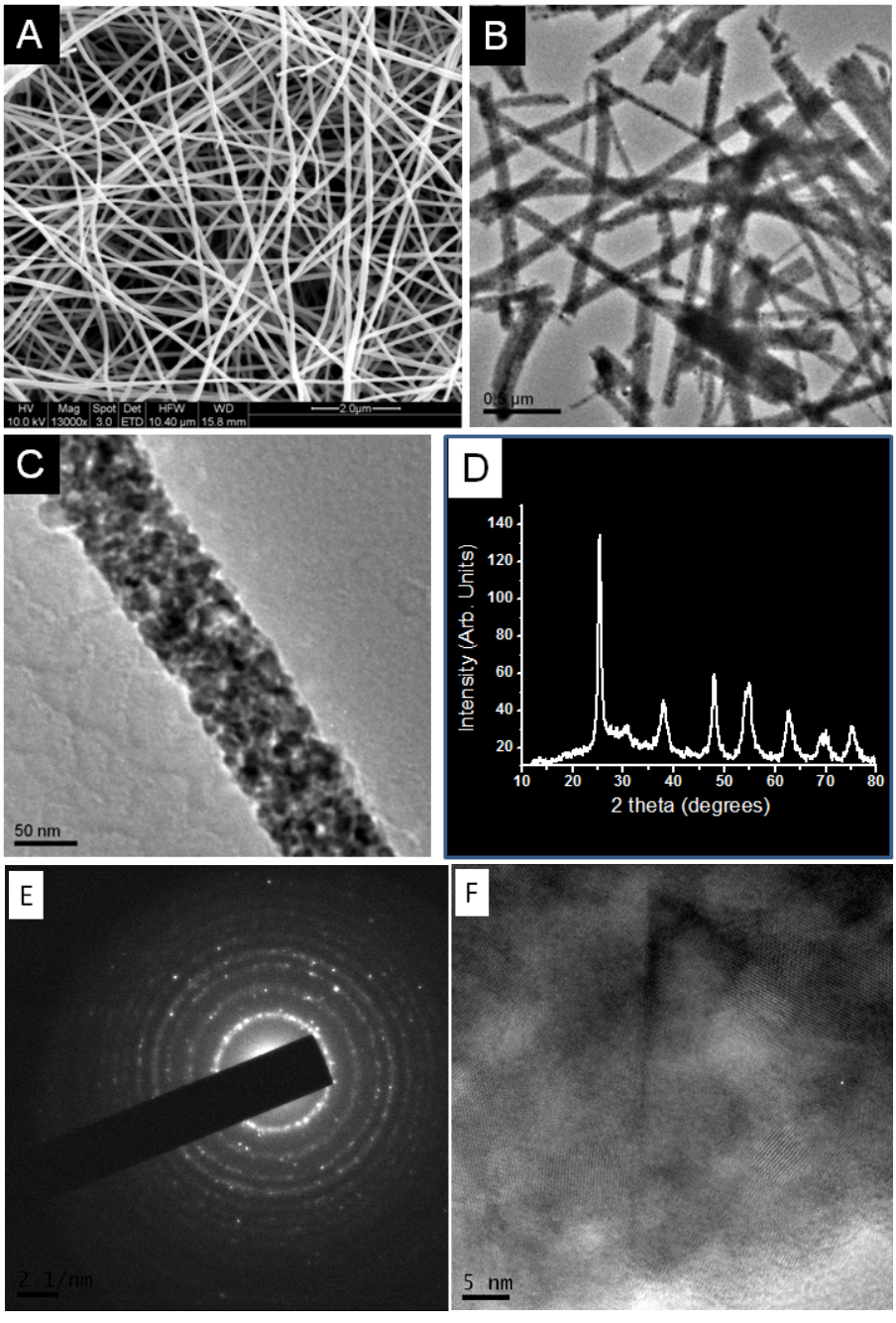
Selected area electron diffraction (SAED) pattern of the TiO_2 meso rice grains showing high-crystallinity of the particles.

Supporting Information (SI) 6



SEM image of the TiO_2 meso rice grains obtained by sintering the TiO_2-PVAc composite (the concentration of PVAc was 16 wt % in solution).

Supporting Information (SI) 7



Representative SEM (Figure A) and TEM (Figures B and C) images of the TiO_2 nanofibers (after sintering) obtained with the TiO_2-PVAc system in DMF. The fibers were continuous and each fiber consists of spherical particles of ~ 10-20 nm size (Figure C). Figure D is the powder X-ray diffractogram of the nanofibers confirming the anatase structure. The anatase structure was further confirmed by SAED (Figure E) and lattice-resolved TEM (Figure F) measurements.