

## Electronic Supplementary Information

# Controlled synthesis of TiO<sub>2</sub> nanoparticles and nanospheres using a microwave assisted approach for their application in dye-sensitized solar cells

M. Ibrahim Dar,<sup>a,b</sup> Aravind Kumar Chandiran,<sup>b</sup> Michael Grätzel,<sup>\* b</sup> Mohammad K. Nazeeruddin,<sup>\* b</sup> and Srinivasrao A. Shivashankar<sup>\* a</sup>

### Chemicals and microwave apparatus

Following chemicals were of analytical grade and were used without further purification: Thiobenzoic acid (90%, Sigma-Aldrich), TiCl<sub>4</sub> (anhydrous, Spectrochem Pvt Ltd), Na metal (sd-fine chem.-limited), benzyl alcohol (Merck), Dimethylformamide (DMF) (Sigma-Aldrich) and absolute ethanol (Commercial Alcohols, Brampton). A single-mode microwave reactor (2.45 GHz, Discover, CEM, USA), which is equipped with a magnetic stirring system, pressure sensor, and an optical fiber temperature sensor was used for the synthesis of TiO<sub>2</sub> nanostructures.

### Experimental Section

*Synthesis of the thiobenzoate complex of titanium:* In a typical synthesis, 470 µL of thiobenzoic acid (4.0 mmol) in methanol was taken in a 100 mL round-bottom flask under flowing Ar. To this reaction mixture, a freshly prepared solution of sodium methoxide [(0.092g, 4.0 mmol) Na in 5 mL MeOH] was added drop-wise at low temperature using an ice bath. Upon stirring, the color of the solution changed to light yellow. Subsequently, TiCl<sub>4</sub> (136 µL, 1.0 mmol in 5 mL MeOH) was added drop-wise, resulting in a white, turbid solution due to the formation of NaCl. After 10-15 min of stirring, the solvent was removed and the reaction mixture was allowed to dry completely under dynamic vacuum, resulting in a dark orange-colored complex. The complex was extracted by the addition of dichloromethane, filtered, and subsequently washed 3-4 times with diethylether. The product finally obtained was stored in argon atmosphere. (Yield 0.546 g, 91%).

## Materials Characterization

The samples were examined by bright-field, high-resolution electron microscopy (HRTEM) and selected area electron diffraction (SAED) in a JEM-2100F field emission transmission electron microscope operating at an accelerating voltage of 200 kV. The TEM specimens were prepared by slow evaporation of diluted solutions, obtained by dispersion of powders in ethanol, and deposited on a formvar-coated copper grid. A field-emission scanning electron microscope (FESEM, Carl Zeiss ULTRA 55) with EDS was employed to analyze the morphology of samples. An electron beam accelerated to 10 kV was used with an in-lens detector. FESEM samples were prepared by dispersing powder sample onto a carbon tape and mounting it on an aluminium specimen holder. Powder X-ray diffraction (XRD) data were collected on a Bruker Advance D8 X-ray diffractometer with a graphite monochromator, using Cu-K $\alpha$  radiation, at a scanning rate of 0.2 deg min<sup>-1</sup>. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific Multilab 2000 system employing Mg K $\alpha$  X-rays as the source ( $h\nu = 1253.437$  eV). Raman spectral studies were performed on a LabRAM HR (UV) instrument at room temperature using an argon-ion laser with an excitation wavelength of 514 nm. A charge-coupled device (CCD) detector was used for sensing the Raman signal. The operating power was chosen as 10 mW with acquisition time 10 sec, a 50X long-working-distance objective (LMPlanFL N 50x/0.5) was used for recording the data.

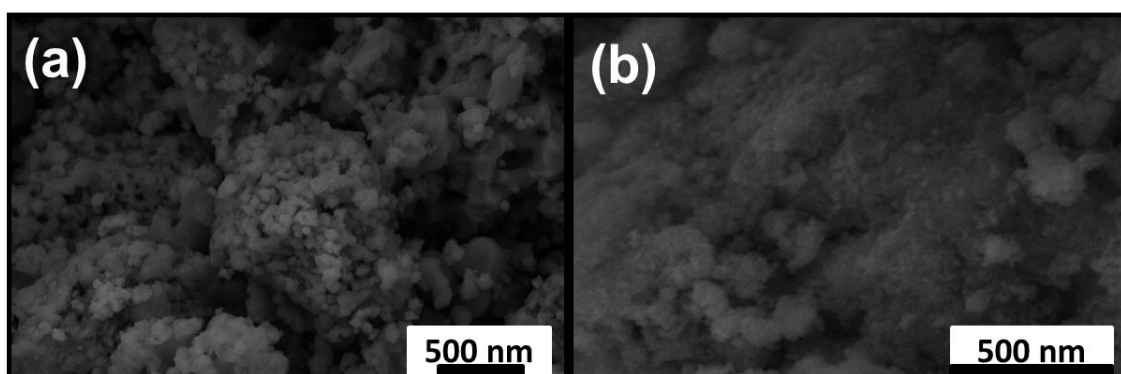
## Photoanode preparation and device fabrication

The TiO<sub>2</sub> paste was obtained by mixing titania powder with terpineol and ethyl cellulose of two different viscosities following the procedure described elsewhere. [Seigo Ito et al, Thin solid films ; Aravind Kumar Chandiran et al., JPCC]. The resulting paste was screen-printed onto a precleaned TCO glass (NSG 10, Nippon sheet glass, Japan) followed by a series of sintering steps (325 °C for 5 min with 15 min ramp time, 375 °C for 5 min with 5 min ramp time, 450 °C for 15 min with 5 min ramp time and 500 °C for 15 min with 5 min ramp time), and the sintered films were used as photoanode. The thickness of the printed film was measured using a KLA Tencor alpha-step 500 surface profilometer and the film

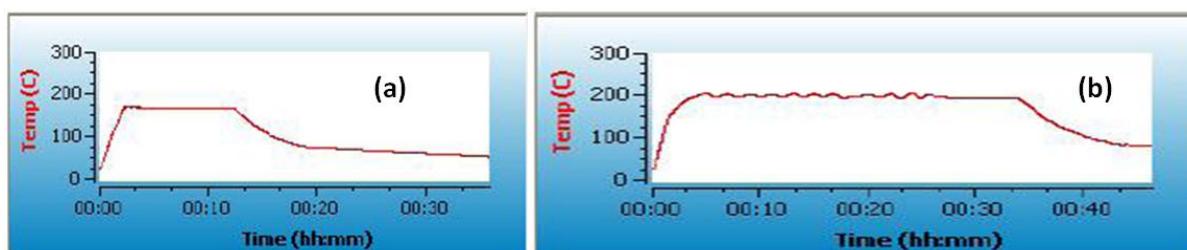
thickness was found to be 8  $\mu\text{m}$ . Following a firing step (500  $^{\circ}\text{C}$ , 30 min),  $\text{TiO}_2$  photoanodes were sensitized in a 0.1 mM **C106** solution in 50/50 (v/v) acetonitrile/t-butanol mixture for 12 hours. The loosely bound dye molecules were removed by washing the sensitized photoanodes in acetonitrile just before cell assembly. The counter electrode was made by thermally depositing Pt at 410  $^{\circ}\text{C}$  for 20 min from a 10 mM  $\text{H}_2\text{PtCl}_6$  (Aldrich) ethanolic solution drop-casted onto FTO glass (TEC7, Solaronix, Switzerland). The two electrodes were melt-sealed using a 25  $\mu\text{m}$ -thick surlyn<sup>TM</sup>(Dupont, USA) polymer film. Our standard iodide/triiodide electrolyte (1M DMII (1,3 – dimethyl imidazolium iodide), 0.03 M  $\text{I}_2$ , 0.1 M GuNCS, 0.5 M t-butyl pyridine and 0.05 M LiI in acetonitrile : valeronitrile (85:15) solvent ) was injected by vacuum back filling technique through a hole on the side of the counter electrodes.

### **Photovoltaic characterization**

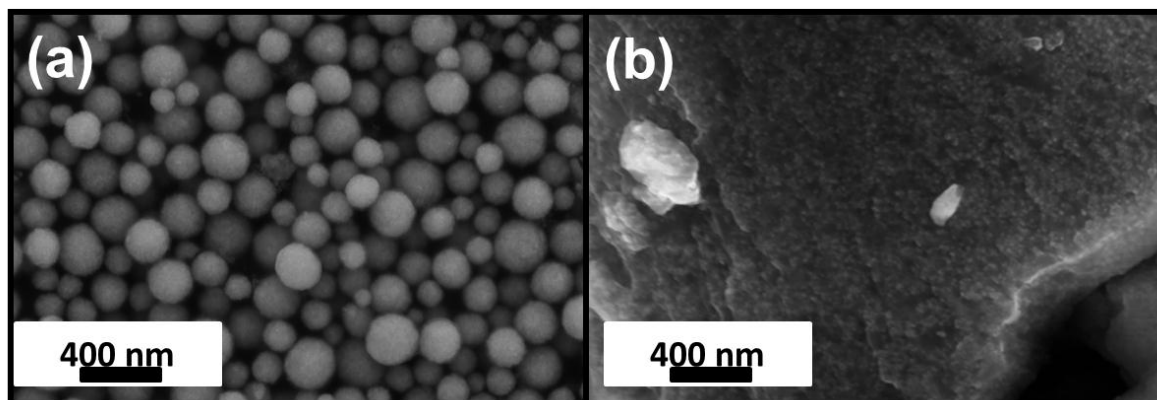
A 450 W xenon lamp (Oriel, USA) was used as the light source for photovoltaic (*J-V*) measurements. The spectral output of the lamp was filtered using a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) to reduce the mismatch between the simulated and actual solar spectrum to less than 2%. The *J-V* characteristics of the cells were recorded with a Keithley model 2400 digital source meter (Keithley, USA). The photo-active area of 0.159  $\text{cm}^2$  was defined using a dark coloured metal mask. Incident photon-to-current conversion efficiency measurements were determined using a 300 W xenon light source (ILC Technology, USA). A double- monochromator spectrometer (Gemini-180, Jobin Yvon Ltd. UK) was used to select and increment the wavelength of the radiation impinging on the cells. The monochromatic incident light was passed through a chopper running at 1 Hz and the on/off ratio was measured by an operational amplifier. This was superimposed on a white light bias corresponding to 10  $\text{mW}/\text{cm}^2$  intensity.



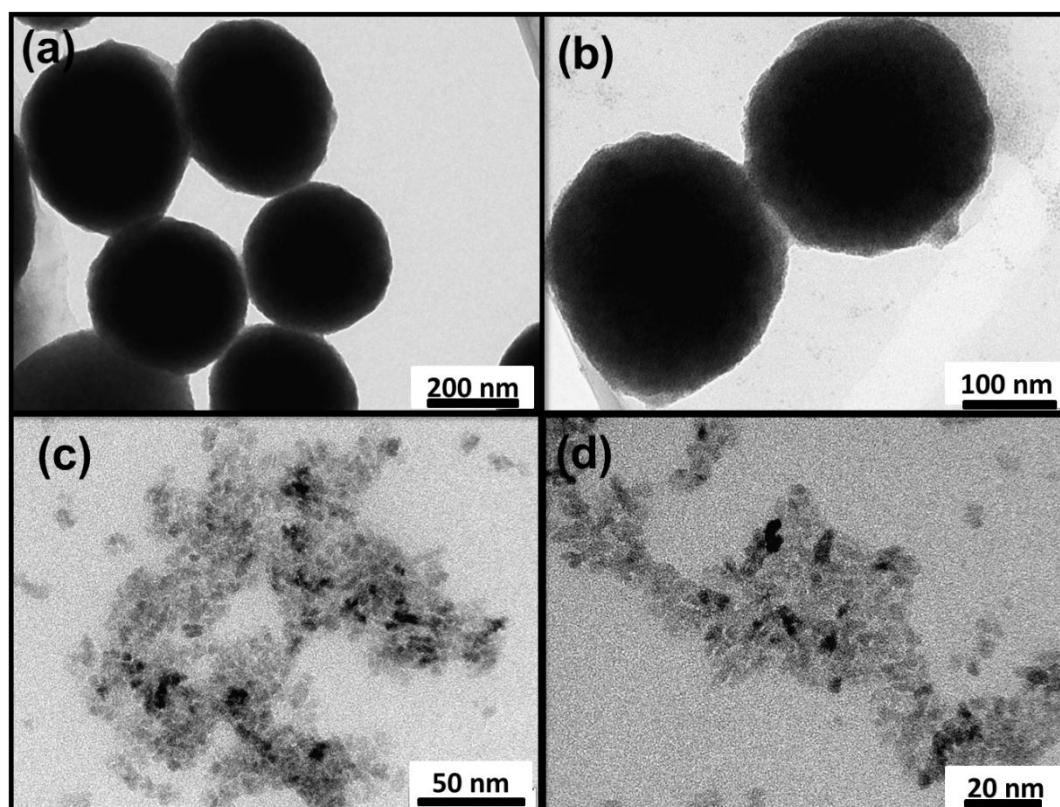
**Fig. S1** FESEM micrographs of anatase TiO<sub>2</sub> nanostructures synthesized using conventional heating (a) Ethanol (b) Benzyl alcohol



**Fig. S2** Temperature profile of the reaction mixtures (a) Ethanol (b) Benzyl alcohol

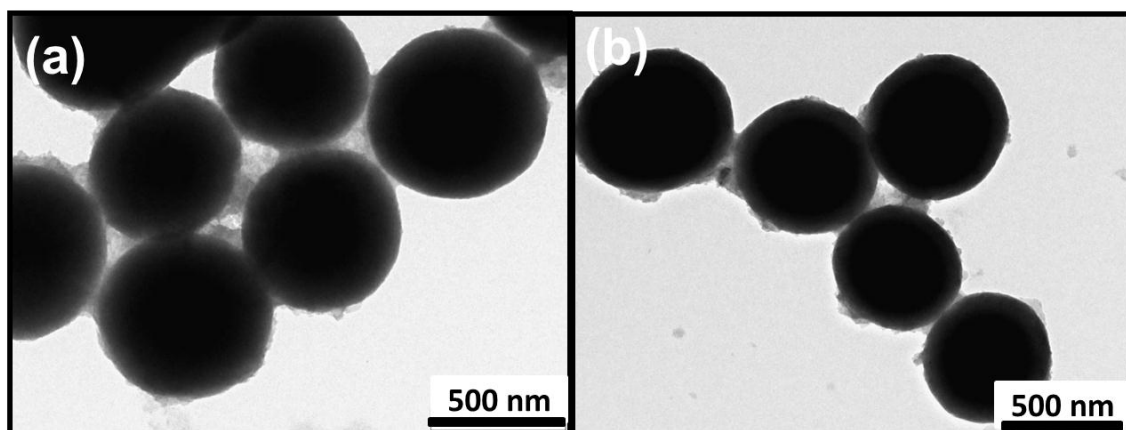


**Fig. S3** FESEM micrographs of anatase TiO<sub>2</sub> nanostructures obtained after increasing the time (a) Ethanol (20 min) (b) Benzyl alcohol (60 min)

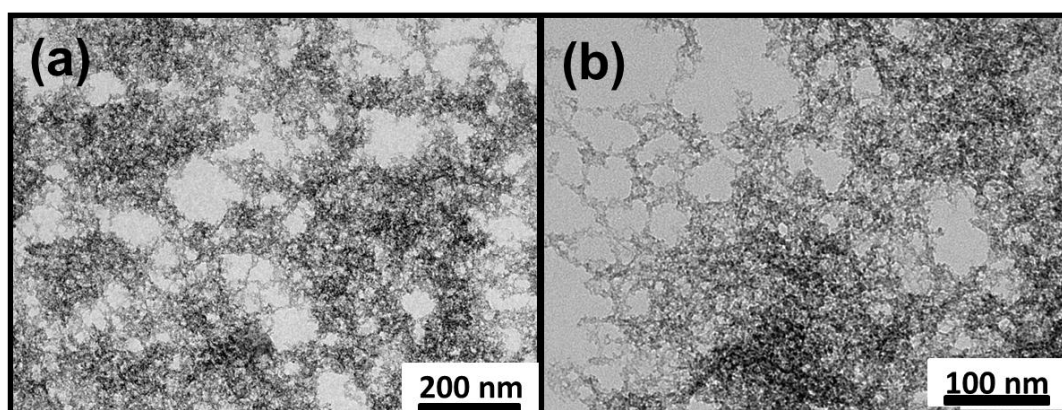


**Fig. S4** TEM micrographs of anatase TiO<sub>2</sub> Nanospheres obtained after using the 150 W (50%) of microwave power (a, b) Ethanol (c,d) Benzyl alcohol.

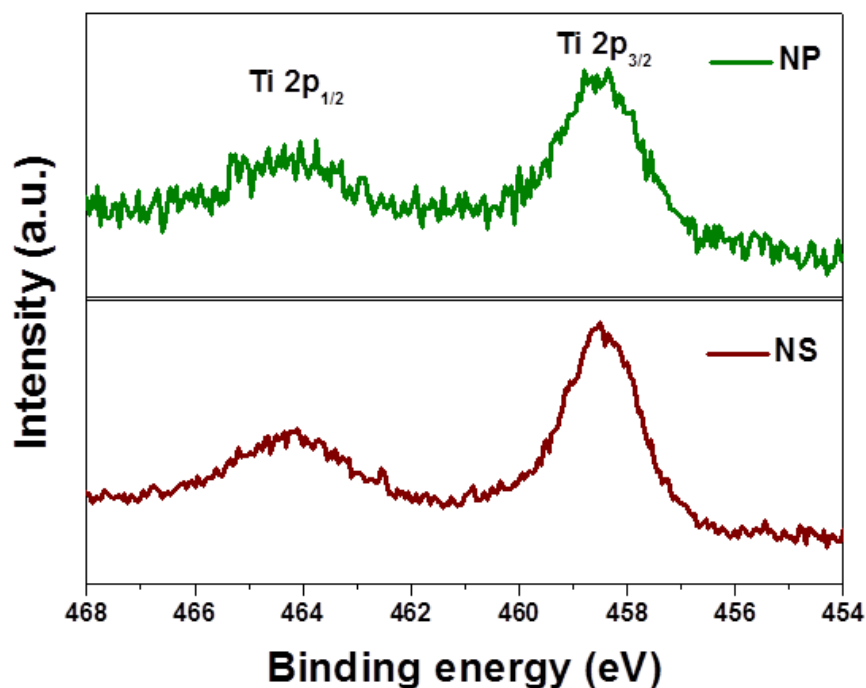




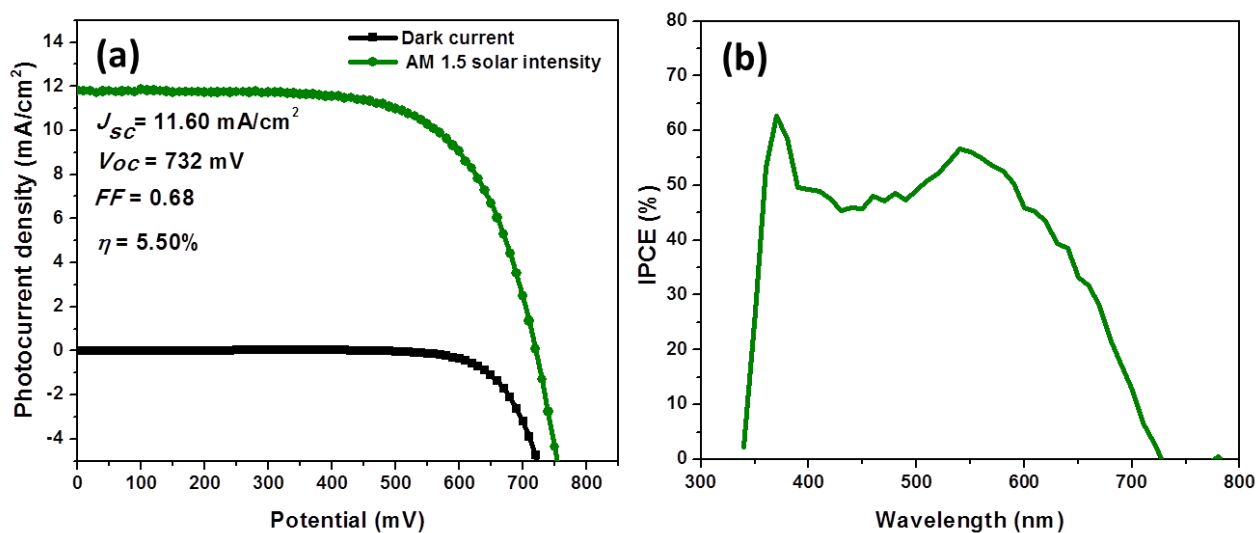
**Fig. S5** TEM micrographs of anatase TiO<sub>2</sub> nanospheres obtained after increasing the concentration of precursor in ethanolic solution.



**Fig. S6** BF-TEM micrographs of anatase TiO<sub>2</sub> nanostructures synthesized using dimethylformamide as solvent.



**Fig. S7** Ti 2p core shell spectra of anatase TiO<sub>2</sub> nanoparticles (NP) and nanospheres (NS).



**Fig. S8** (a) Current-voltage (J-V) characteristics under dark and irradiation at  $100 \text{ mWcm}^{-2}$  photon flux and the IPCE spectrum (b) as a function of the wavelength of monochromatic light for the device containing only transparent (NP) layer.