

Electronic Supporting Information

Electrophoretic deposition of mesoporous TiO₂ nanoparticles consisting of primary anatase nanocrystallites on a plastic substrate for flexible dye-sensitized solar cells

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1. Materials

Lithium iodide (LiI) and iodine (I₂) were obtained from Merck; acetonitrile (ACN), 3-methoxypropionitrile (MPN), and tertiary butanol were also obtained from Merck and their water molecules were removed by molecular sieves (4 Å). 4-tert-butylpyridine (TBP) and tert-butyl alcohol were obtained from Acros; ethanol, neutral cleaner and isopropyl alcohol (IPA) were obtained from Aldrich. TiO₂ powders (P90, 14 nm, 99.9% anatase) were obtained from Degussa. FTO glass (15 Ω Sq.⁻¹) was obtained from Solaronix S. A., Aubonne, Switzerland. ITO-PEN (13 Ω Sq.⁻¹) was purchased from Peccell Technologies, Inc..

2. Synthesis and crystallization of MTNs

Typically, 2.2 mL of titanium(IV) ethoxide (Ti(OC₂H₅)₄, Aldrich) was added drop by drop into 100 mL of ethanol (98%, Aldrich) while vigorous stirring at room temperature. After stirring until white precipitate appears (usually around 30 mins), the whole suspension was kept in a static condition at room temperature for at least 24 h. Then, the precipitate was collected by centrifuge (5000 rpm for 10 min), washed by ethanol several times, and dried in a vacuum.

The as-synthesized MTNs (1 g) and H₂O (75 mL) were placed into an autoclave, and the autoclave was heated in an oven at 180 °C for 12 h. After reacting overnight,

the sample was washed with DI water and dried in vacuum. This post hydrothermal treatment would change the crystalline phase of the as-synthesized MTNs from amorphous phase to anatase phase.

3. *Characterization of the synthesized MTNs*

The structural properties of the samples were analyzed by X-ray diffraction (XRD) on a Rigaku ultima IV with Cu K α radiation (40 kV, 40 mA) with a 2 θ range of 20 to 80 degrees in a scan speed of 100 degree min⁻¹ and a step scan size of 0.02 degree. The morphology and porous structure of the samples were observed with scanning electron microscopy (SEM, NovaTM Nano SEM, operating at 10 kV) and transmission electron microscopy (TEM, JOEL JEM-1230 electron microscope, operating at 100 kV and photographed with a Gatan DualVision CCD Camera). For SEM observation, we took SEM images of the deposited MTNs and P90 films from top view. For TEM observation, the MTNs or P90 was first dispersed in ethanol and dropped onto copper grids. The porous properties of the products were analyzed using N₂ adsorption/desorption isotherms on a Micromeritics ASAP 2000 instrument. Samples were degased at 100 °C overnight before N₂ adsorption. Specific surface area was evaluated using the Brunauer-Emmett-Teller (BET) method at P/P₀ = 0.14-0.99, and the average pore size was calculated from the desorption isotherm using the Barret-Joyner-alenda (BJH) method, as shown in Fig. S2. The BET specific surface area for the MTNs and P90 were calculated at P/P₀ = 0.19858 with 132.7042 m² g⁻¹ and at P/P₀ = 0.20022 with 91.3 m² g⁻¹, respectively.

4. *Preparation of the TiO₂ suspension and the photoanode*

The MTNs and commercial nanocrystalline P90-TiO₂ powder were dispersed well in isopropyl alcohol (IPA) at 3 g L⁻¹, without using any surfactant or additive. The suspension was stirred for at least 3 h and then ultrasonicated for 20 min. After ultrasonication the TiO₂ suspension was put in a container for electrophoresis; an FTO glass was used as the anode and a conducting plastic substrate (13 Ω Sq.⁻¹, ITO-PEN film, Peccell Technologies, Inc.) as the cathode during the EPD process. The EPD was performed at a DC electric field of 200 V cm⁻¹ for 1 min. After finishing the EPD process, the residual IPA solvent on the as-deposited film was evaporated for a few seconds in air at ambient temperature. As the post-treatment of the nanostructured TiO₂ film obtained by the EPD process, the static mechanical compression (MTS-810, Material Testing System, Eden Prairie, MN, USA) was applied at a specific pressure of 100 MPa. The TiO₂ photoelectrodes were following immersed in a 3 \times 10⁻⁴ M solution of N719 (Solaronix S. A., Aubonne, Switzerland) in acetonitrile and tert-butyl alcohol (volume ratio of 1:1) at 40 °C for 4 h. The TiO₂ photoelectrodes

prepared as described above was coupled with a platinum counter electrode (PE-CE) made of ITO-PEN with Pt sputtered for 3 min. The photoelectrodes were separated by a 25 μm -thick Surlyn tape (SX1170-25, Solaronix S.A., Aubonne, Switzerland) and sealed by heating. The electrolyte was injected into the gap between the two electrodes by capillarity; the electrolyte-injecting hole was previously made in the counter electrode with a drilling machine, and the hole was sealed with hot-melt glue after the electrolyte injection. The working area of the photoanode was confined by a mask (0.55 cm in diameter). And the electrolyte is composed of 0.4 M LiI (lithium iodide), 0.02 M I₂ (iodine), 0.4 M TBAI (tetrabutylammonium iodide) and 0.3 M NMB (N-methylbenzimidazole) in acetonitrile (ACN).

5. Instrumentation

The surface of the DSSC was illuminated by a class A quality solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc.) and the incident light intensity of 100 mW cm^{-2} was calibrated with a standard Si Cell (PECSI01, Peccell Technologies, Inc.). The photoelectrochemical characteristics and electrochemical impedance spectra (EIS) of the cells were recorded using a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands), under 100 mW cm^{-2} light intensity. The frequency range explored for the impedance measurements was from 10 mHz to 65 kHz. The applied bias voltage was set at the open-circuit voltage of the DSSC, between the ITO-PEN-Pt-CE and the ITO-PEN-TiO₂-dye working electrode, starting from the short-circuit condition; the corresponding AC amplitude was 10 mV. Morphologies of the films were observed by scanning electron microscopy (SEM, Nova NanoSEM 230, FEI Ultra-High Resolution FE-SEM with low vacuum mode) and transmission electron microscopy (TEM, JOEL JEM-1230 electron microscope, operating at 100 kV and photographed with a Gatan DualVision CCD Camera). X-Ray diffraction patterns (XRD, X'Pert, PANalytical, the Netherlands) with Cu K α radiation were used for the phase identification of the TiO₂ powders. The film thickness was determined using a surface profilometer (Sloan Dektak 3030). The size of the TiO₂ photoanode was adjusted by scrapping the edges of the film with a cotton swap rinsed with ethanol; the cell was covered with a mask during the obtainment of the *J-V* curves. The incident-photo-to-current efficiency (IPCE) data for the DSSCs were collected using a solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc.) in coupled with a monochromator (Oriel 74100) to selectively filter the desired wavelength. The diffuse reflectance spectra were measured using a Jasco V-670 spectrometer equipped with an integrating sphere (ISN-723 60 mm) accessory.

Results

Fig. S1

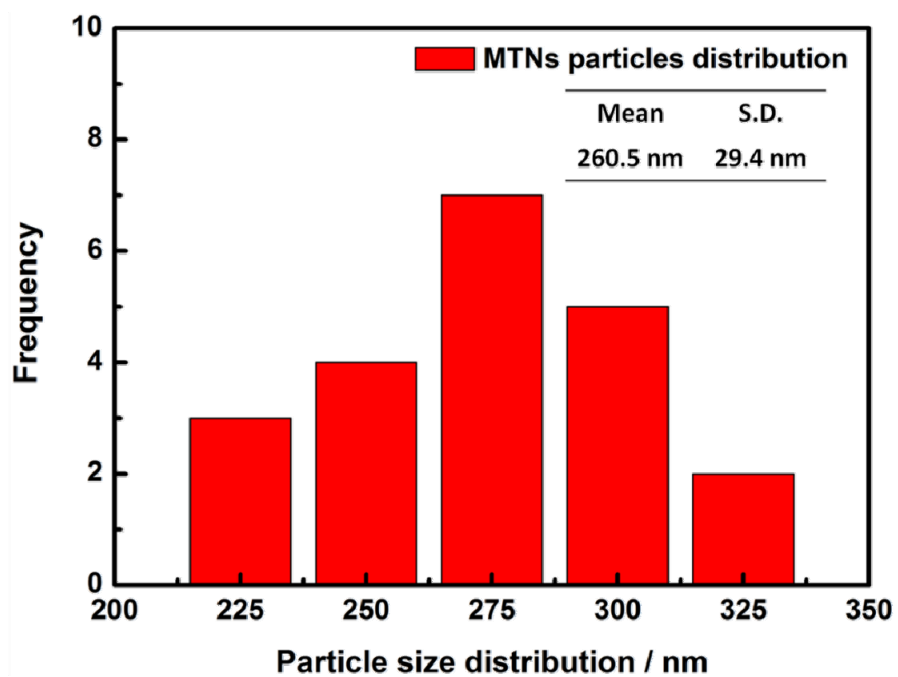


Fig. S1 Particles size distribution of MTNs. 21 particles were counted for this calculation.

Fig. S2

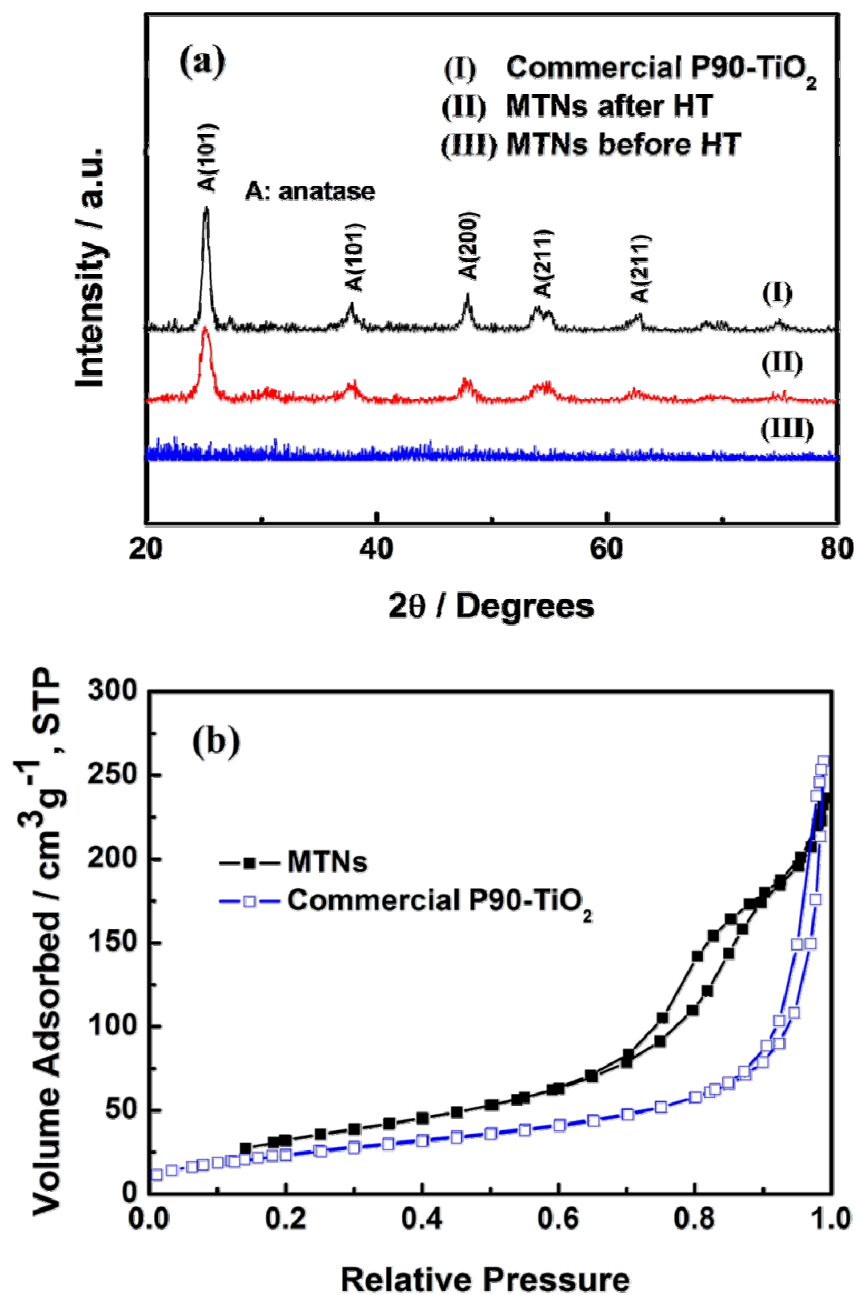


Fig. S2 (a) XRD patterns and (b) nitrogen adsorption-desorption isotherms for P90 TiO₂ nanoparticles and MTNs (before and after hydrothermal treatment).

Fig. S3

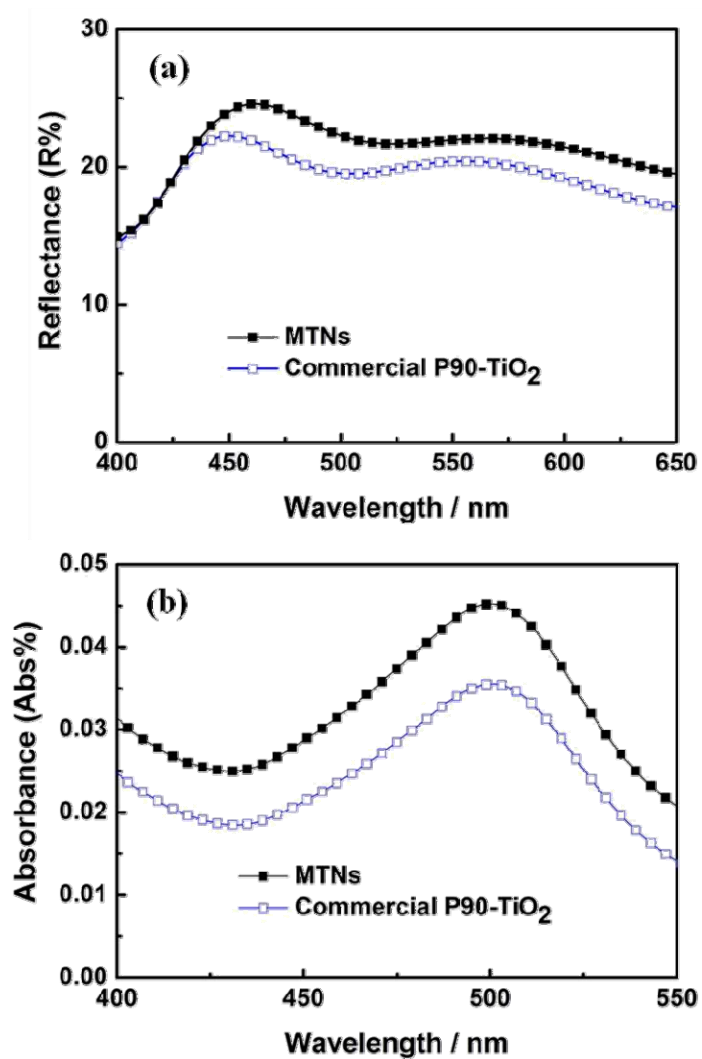


Fig. S3 (a) The UV-visible diffuse reflectance and (b) absorption spectra of the dye-containing NaOH solutions. The dye molecules were washed from the photoanodes.