

Electronic Supplementary Information

Graft Copolymer Directed Synthesis of Micron-Thick Organized Mesoporous TiO₂ Films for Solid-State Dye-Sensitized Solar Cells

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Experimental

Materials

Poly(vinyl chloride) (PVC, $M_w = 97,000$ g/mol, $M_n = 55,000$ g/mol), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol) methyl ether methacrylate, $M_n = 475$ g/mol), titanium(IV) isopropoxide (TTIP, 97%), hydrogen chloride solution (HCl, 37 wt%), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA, 99%), copper(I) chloride (CuCl, 99%), fumed silica nanoparticles (SiO₂, 14 nm), poly(ethylene glycol dimethyl ether) (PEGDME, $M_n = 500$ g/mol), poly(3,4-ethylenedioxy thiophene)-poly(styrene sulfonate) (PEDOT-PSSA), 2.2-2.6% in H₂O, (high-conductivity grade), lithium bistrifluoro methanesulfonamide (LiTFSI) and iodine (I₂) were purchased from Aldrich. 1-Methyl-3-propyl imidazolium iodide (MPII, C₇H₁₃N₂I) and ruthenium dye (535-bisTBA, N719) were

purchased from Solaronix, Switzerland. Tetrahydrofuran (THF), N-methyl pyrrolidone (NMP), and methanol were obtained from J.T. Baker. All solvents and chemicals were reagent grade and used as received.

Synthesis of the graft copolymer

Six grams of PVC was dissolved in 50 mL of NMP by stirring at 90 °C for 4 h. After cooling the solution to room temperature, 15 g of POEM, 0.1 g of CuCl, and 0.23 mL of HMTETA were added to the solution. The green mixtures were stirred until homogeneous, and were purged with nitrogen for 30 min. The reaction was carried out at 90 °C for 18 h. After polymerization, the resultant mixtures were diluted with THF. After passing the solutions through a column with activated Al₂O₃ to remove the catalyst, the solutions were precipitated into methanol. The grafted copolymers were purified by dissolving in THF and reprecipitating into methanol three times. PVC-g-POEM graft copolymer with a PVC:POEM = 4:6 wt ratio was obtained in a powder form and dried in a vacuum oven overnight at room temperature.

Preparation of the organized mesoporous TiO₂ films

The titania precursor solution was prepared to have a mole ratio of TTIP:water:HCl = 2:1:1. A solution was prepared by slowly adding HCl (37 wt%) to TTIP under vigorous stirring. Additional deionized (DI) water was slowly added to the TTIP solution. Separately, 0.2 g of PVC-g-POEM graft copolymer was dissolved in 2 ml of THF. The concentration of polymer solution was increased compared to a previous study^[1] because the viscous graft copolymer solution is expected to play a role as a structure directing agent to enhance the hydrogen bonding interaction between polymer and TTIP; thereby increasing the viscosity of the

polymer solution. The ratio of polymer solution to precursor solution was controlled from 20vol% to 40vol% to show the role of titania precursor relative to nanocrystalline TiO₂. Degussa P25 nanocrystalline particles were added to the solution at 5wt%, and stirred for 3 hours to obtain a white solution. The films were deposited onto a FTO conducting glass using a doctor blade method. After calcination at 450 °C for 30 min, the organic chemicals were completely removed to produce the mesoporous TiO₂ films. The organized mesoporous TiO₂ films derived from the 20, 30, 40 vol% TTIP solutions are referred to as “meso1,” “meso2,” and “meso3,” respectively, in this article.

Characterization

Morphologies of the mesoporous TiO₂ films were observed using field-emission scanning electron microscopy (FE-SEM, AURIGA, Carl Zeiss, Germany). The specific surface area, average pore diameter, specific pore volume, and average particle diameter of TiO₂ films were measured at the N₂ adsorption-desorption isotherm by the Brunauer-Emmett-Teller (BET, for specific surface area) and Barrett-Joyner-Halenda (BJH, for specific pore volume and average pore diameter) methods using BELSORP-MAX after drying the sample at room temperature for one day in a vacuum oven. Prior to the taking of these measurements, the TiO₂ films were additionally degassed at 70°C under dynamic vacuum (10⁻² Torr) for 1 hour.

Fabrication of the DSSCs

DSSCs were fabricated according to the previously reported procedure.^[1-4] Transparent SnO₂/F-layered conductive glass (FTO, Pilkington. Co. Ltd., 8 ohms/sq, 2.3 mm thick) was employed in order to prepare both the photo and counter electrodes. The dense TiO₂ film with 100 nm thickness as a blocking layer was prepared by spin coating a titanium(IV) bis(ethyl

acetoacetato) diisopropoxide solution (2 wt% in butanol) at 1500 rpm for 10 sec, followed by calcination at 450°C for 30 min. Then, commercial TiO₂ paste (Ti-Nanoxide D20, Solaronix) or sol-gel solutions containing the graft copolymer and different ratios of TTIP solution were deposited onto the FTO glass a doctor-blade technique, followed by successive sintering at 450 °C for 30min. The mesoporous TiO₂ films were sensitized overnight in a Ru(dcbpy)₂(NCS)₂ dye (dcbpy=2,2-bipyridyl-4,4-dicarboxylato) solution (535-bisTBA, Solaronix, 13 mg, dissolved in 50 g distilled ethanol). Pt layered counter-electrodes were prepared by spin-coating a 1wt% H₂PtCl₆ solution in isopropanol onto the FTO glass and then sintering the film at 450 °C for 30 min. Polymer electrolyte solutions consisting of PEGDME, SiO₂, MPII and I₂ dissolved in THF were cast onto a dye-adsorbed TiO₂ electrode and evaporated very slowly to allow penetration of the electrolytes through the mesopores of the TiO₂ layer. Both electrodes were then superposed together and pressed between two glass plates in order to achieve both slow evaporation of the solvent and a thin electrolyte layer. The cells were placed in a vacuum oven for 1 day for complete evaporation of the solvent. To further investigate the pore filling ability of organized mesoporous TiO₂ films, the large M_w solid-state electrolyte, i.e., PVC-g-POEM, and the hole transport material, PEDOT-PSSA, were tested. The casting method and procedures of PVC-g-POEM electrolyte were similar to the PEGDME/SiO₂/MPII/I₂ electrolyte. In the case of PEDOT-PSSA, a small amount of LiTFSI salt and MPII were dropped onto the PEDOT-PSSA casted TiO₂ photoelectrode.

The photoelectrochemical performance, including the short-circuit current (J_{sc} , mA/cm²), open-circuit voltage (V_{oc} , V), fill factor (FF), and overall energy conversion efficiency (η) were measured using a Keithley Model 2400 source meter and a 1000 W xenon lamp (Oriol, 91193). The light was homogeneous up to an 8 × 8 in² area and its intensity was calibrated with a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si+KG

filter, Certificate No. C-ISE269) for 1 sun light intensity, 100 mW/cm²). The intensity was verified with a NREL-calibrated Si solar cell (PV Measurements Inc.). Photoelectrochemical performance was calculated using the following equations:

$$FF = \frac{V_{\max} \cdot J_{\max}}{V_{oc} \cdot J_{sc}} \quad (1)$$

$$\eta(\%) = \frac{V_{\max} \cdot J_{\max}}{P_{in}} \times 100 = \frac{V_{oc} \cdot J_{sc} \cdot ff}{P_{in}} \times 100 \quad (2)$$

where J_{sc} is the short-circuit current density (mA/cm²), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} (mA/cm²) and V_{max} (V) are the current density and voltage in the J - V curve, respectively, at the point of maximum power output.

Electrochemical impedance spectroscopy (EIS) analysis was used to investigate the internal resistance and electron charge-transfer kinetics of TiO₂ photoelectrodes in DSSCs. EIS measurements were carried out at frequencies ranging from 0.01 Hz to 0.1 MHz with an AC amplitude of 0.02 V under one-sun illumination.

Measurement of dye adsorption

First, the N719 dye-sensitized TiO₂ photoelectrode was dipped into 10.0 mL of a 10⁻² M solution of NaOH in ethanol-H₂O (1:1). The mixture was stirred until complete desorption of the dye into the liquid occurred. The volume of the NaOH solution containing the fully desorbed dye was then carefully measured by UV-visible spectroscopy. The amounts of the NaOH solutions were recorded, and the absorption value at 515 nm (as a function of wavelength) was used to calculate the number of adsorbed N719 dye molecules according to the Beer-Lambert law, $A = \epsilon lc$, where A is the absorbance of the UV-visible spectra at 515

nm, $\epsilon = 14,100/\text{M cm}$ is the molar extinction coefficient of the dye at 515 nm, l is the path length of the light beam, and c is the dye concentration.^[5]

1. S. H. Ahn, J. H. Koh, J. A. Seo, J. H. Kim, *Chem. Commun.* 2010, **46**, 1935.
2. S. H. Ahn, H. Jeon, K. J. Son, H. Ahn, W. G. Koh, D. Y. Ryu, J. H. Kim, *J. Mater. Chem.* 2011, **21**, 1772.
3. D. K. Roh, J. T. Park, S. H. Ahn, H. Ahn, D. Y. Ryu, J. H. Kim, *Electrochim. Acta* 2010, **55**, 4976.
4. J. T. Park, D.K. Roh, R. Patel, E. Kim, D.Y. Ryu, J.H. Kim, *J. Mater. Chem.* 2010, **20**, 8521.
5. Z.S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, *Coord. Chem. Rev.* 2004, **248**, 1381.

Fig. S1. J-V curves of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and low M_w polymer electrolytes (PEGDME/ SiO_2 /MPII/ I_2).

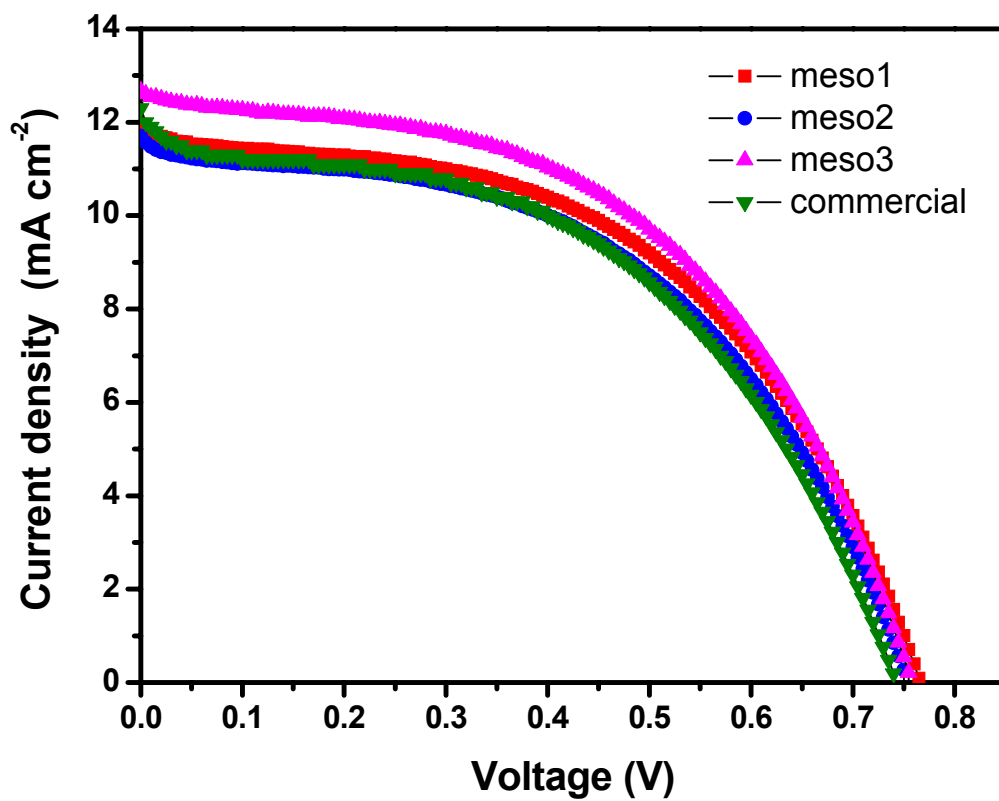
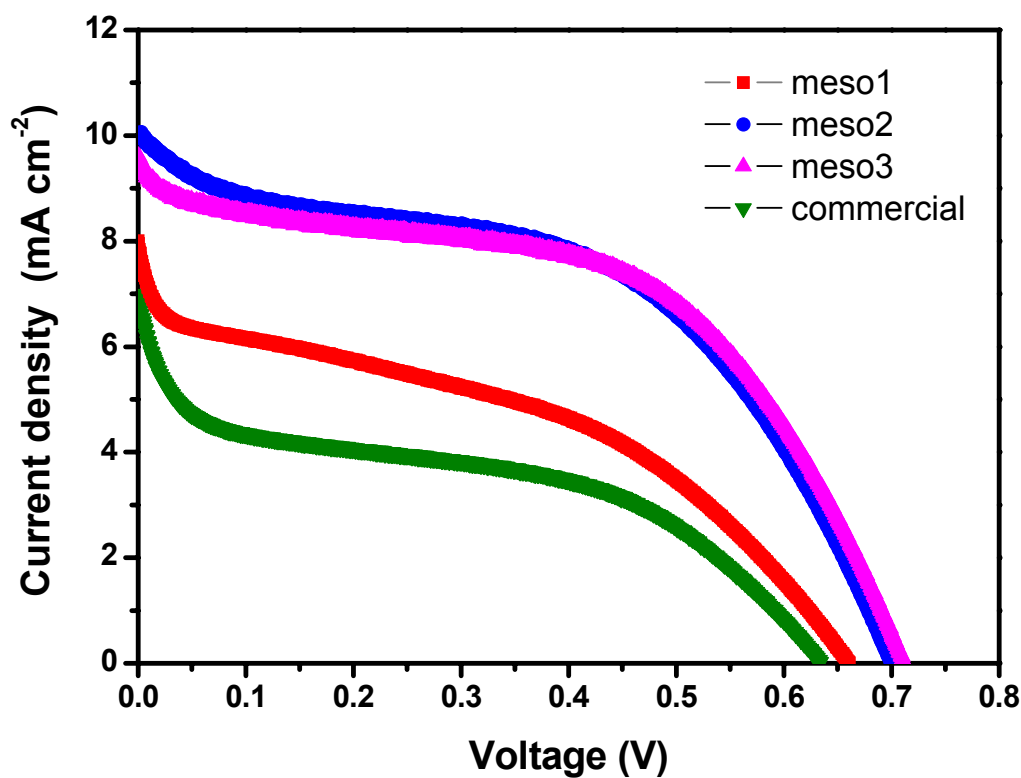


Fig. S2. J-V curves of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and high M_w polymer electrolytes (PVC-g-POEM/MPII/I₂).



A slight decrease in current at low voltages is presumably related to insufficient penetration of large molecular weight polymer electrolytes, although it was not observed in cross-sectional SEM images of Fig. S5.

Fig. S3. J-V curves of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and hole-transport material (PEDOT/PSSA/LiTFSI/MPII).

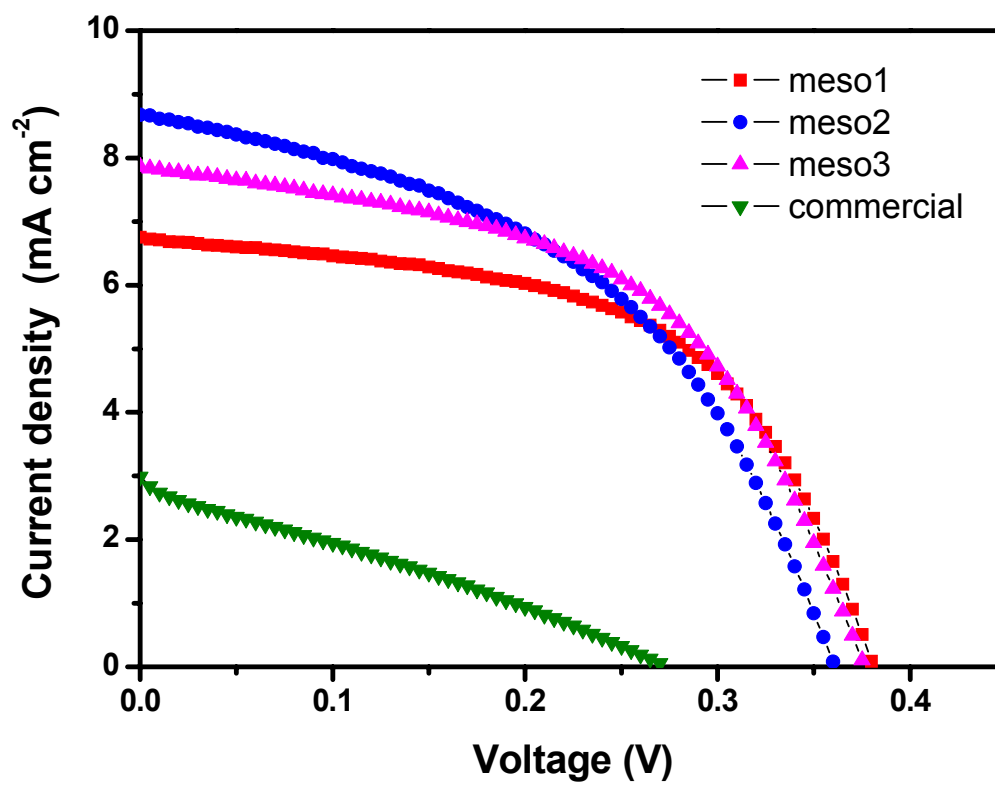


Fig. S4. EIS results of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and low M_w polymer electrolytes (PEGDME/ SiO_2 /MPPII/ I_2); (a) Nyquist plot and (b) Bode phase plot.

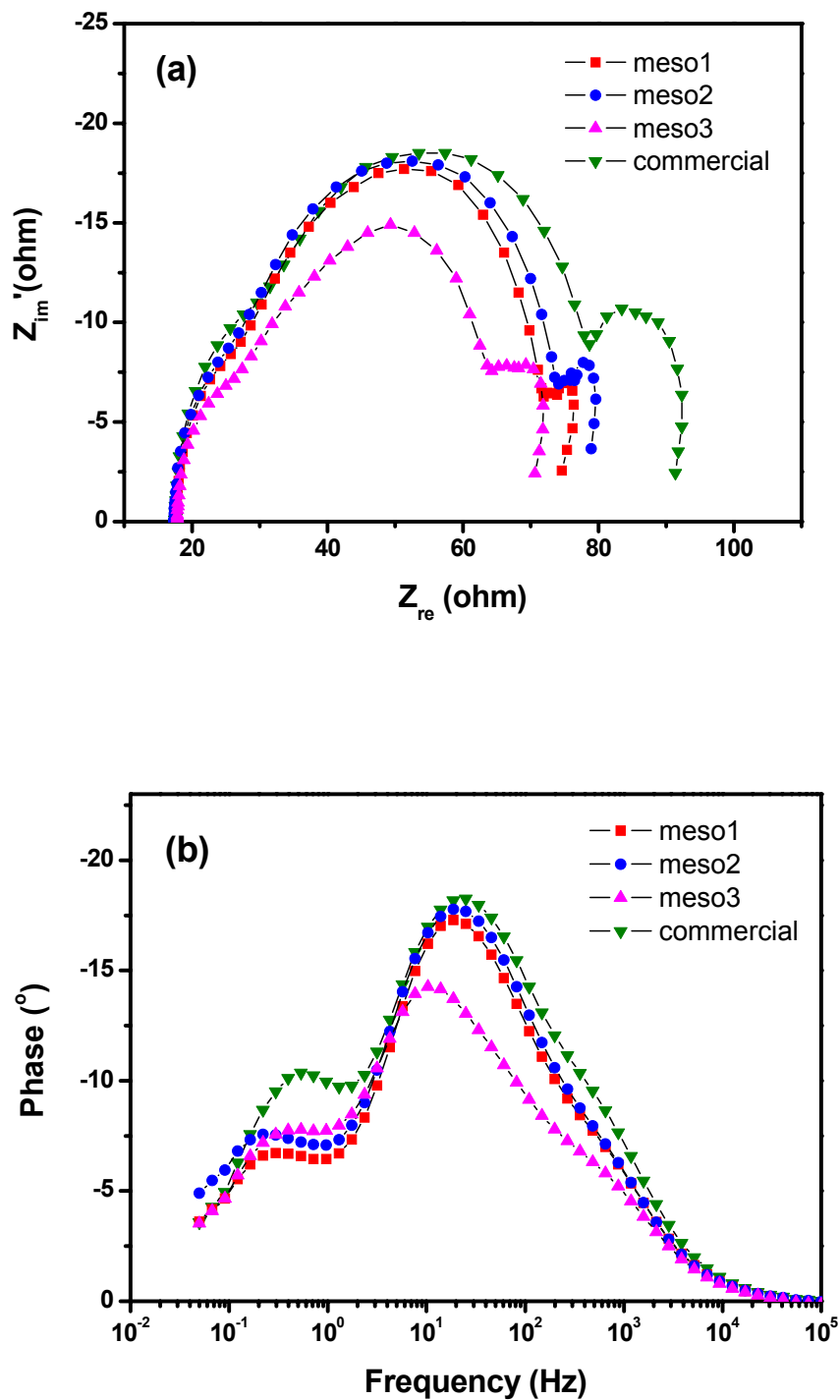
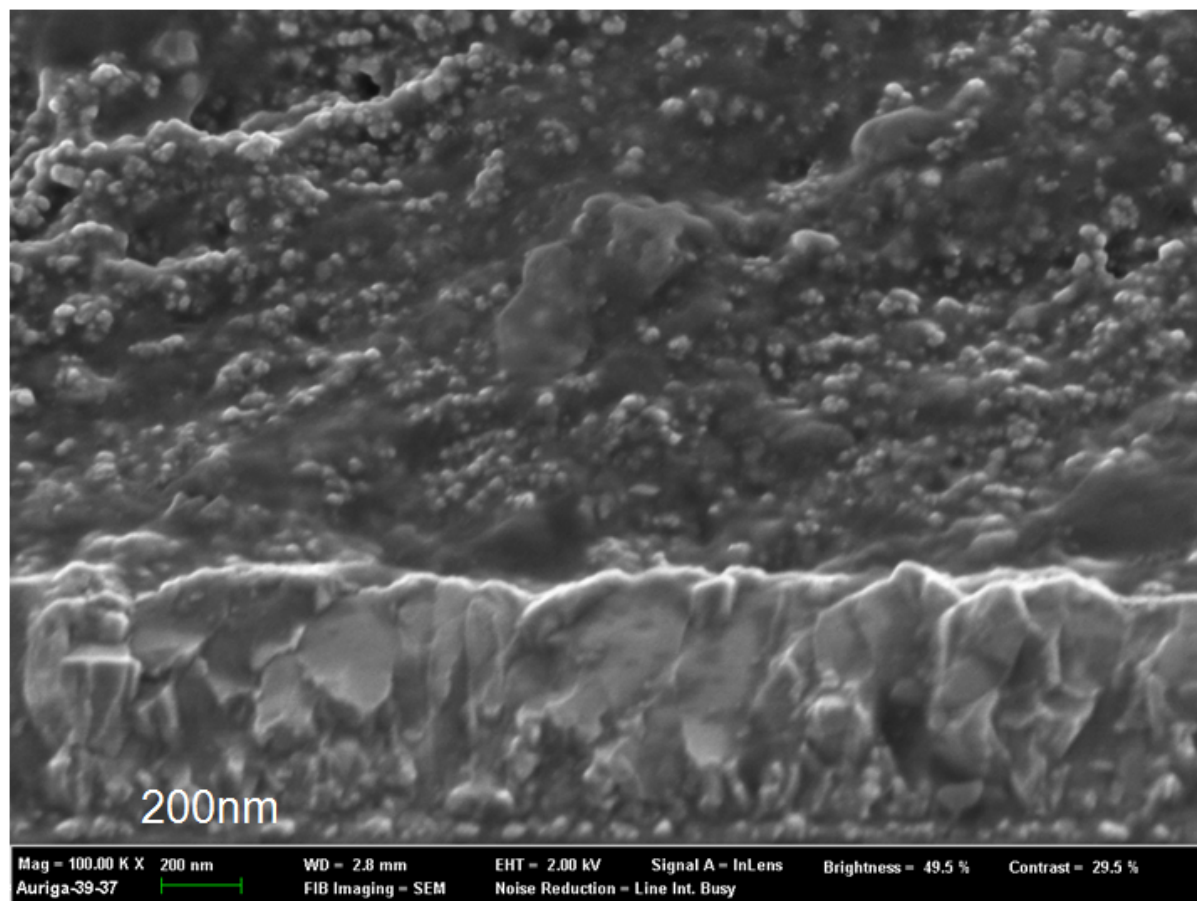


Fig. S5. Cross-sectional SEM images of 6 μm thick organized mesoporous TiO_2 films infiltrated with high M_w polymer electrolytes (PVC-g-POEM/MPII/I₂).



A more convincing proof is to perform mass-based measurements to derive the mass of polymer deposited and based on the porosity, determine quantitatively the level of pore filling. Lau group (*Nano Lett.* 2011, **11**, 419-423) introduced the combined method of thermogravimetric analysis (TGA) and N_2 sorption measurements for measuring pore filling as a more quantitative means. In addition, McGehee and Gratzel group (*Adv. Funct. Mater.* 2009, **19**, 2431) quantified pore filling using X-ray photoelectron spectroscopy (XPS) depth profiling and UV-visible spectroscopy.

Fig. S6. Dark current of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and low M_w polymer electrolytes (PEGDME/ SiO_2 /MPII/ I_2).

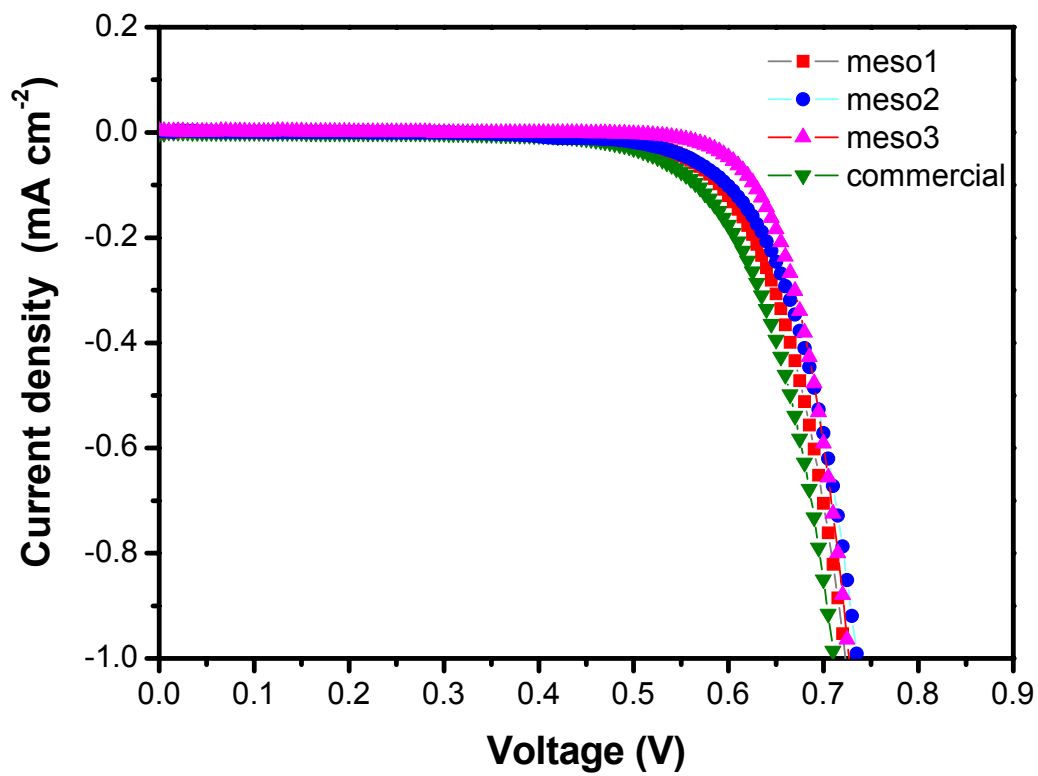


Fig. S7. Example of pore size measurement of TiO₂ Films using the soft-ware of FE-SEM (AURIGA, Carl Zeiss, Germany).

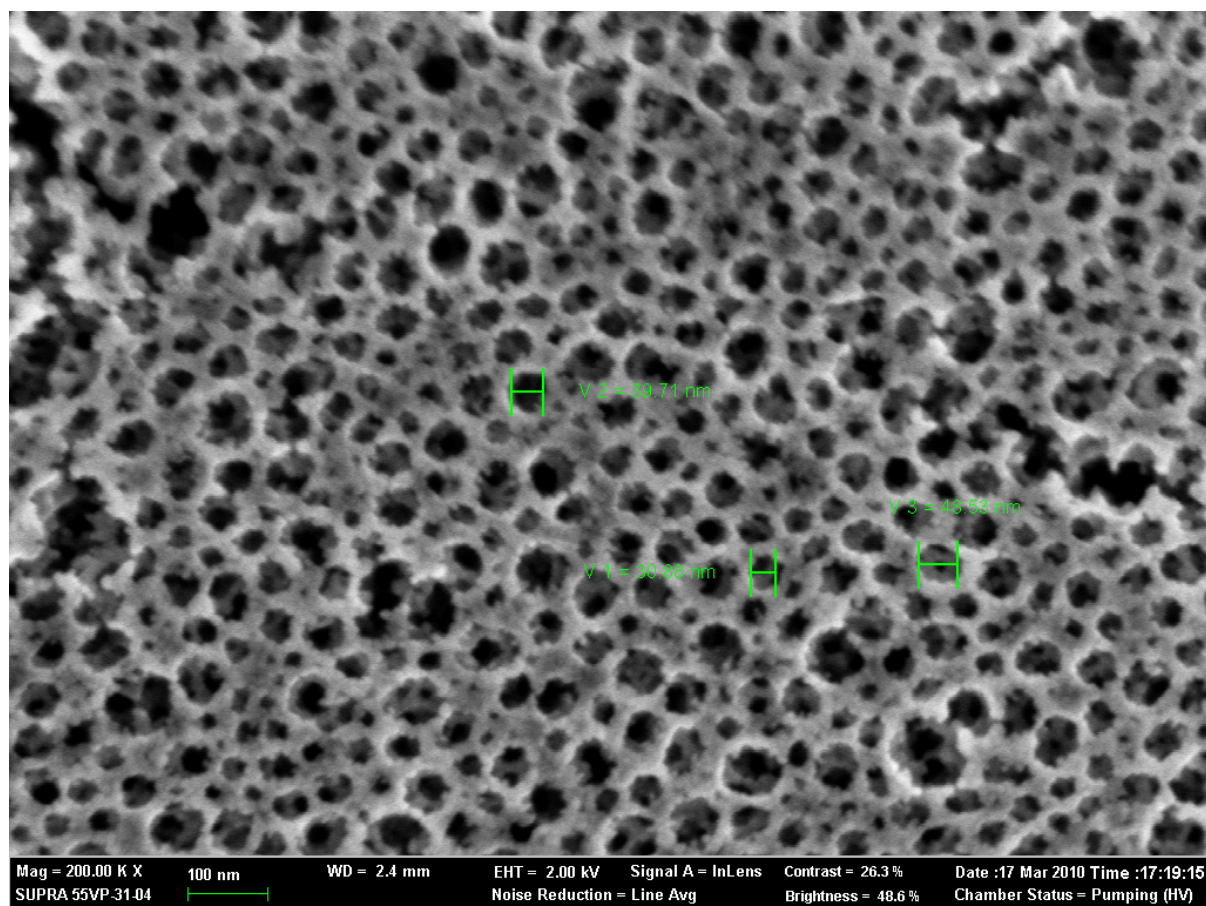


Table S1. Performance parameters of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and low M_w polymer electrolytes (PEGDME/ SiO_2 /MPII/ I_2).

| | V_{oc} (V) | J_{sc} (mA/cm^2) | FF | Efficiency (%) |
|------------|-----------------|---|------|----------------|
| meso1 | 0.77 | 11.9 | 0.50 | 4.6 |
| meso2 | 0.76 | 11.7 | 0.49 | 4.4 |
| meso3 | 0.76 | 12.7 | 0.51 | 4.9 |
| commercial | 0.74 | 12.3 | 0.47 | 4.3 |

Table S2. Performance parameters of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and high M_w polymer electrolytes (PVC-g-POEM/MPII/ I_2).

| | V_{oc} (V) | J_{sc} (mA/cm^2) | FF | Efficiency (%) |
|------------|-----------------|---|------|----------------|
| meso1 | 0.66 | 8.0 | 0.35 | 1.8 |
| meso2 | 0.70 | 10.1 | 0.46 | 3.3 |
| meso3 | 0.71 | 9.6 | 0.49 | 3.3 |
| commercial | 0.63 | 7.0 | 0.31 | 1.4 |

Table S3. Performance parameters of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and hole-transport material (PEDOT/PSSA/LiTFSI/MPII).

| | V_{oc} (V) | J_{sc} (mA/cm^2) | FF | Efficiency (%) |
|------------|-----------------|---|------|----------------|
| meso1 | 0.38 | 6.75 | 0.55 | 1.4 |
| meso2 | 0.36 | 8.68 | 0.46 | 1.4 |
| meso3 | 0.38 | 7.86 | 0.51 | 1.5 |
| commercial | 0.27 | 2.99 | 0.27 | 0.2 |

Table S4. Electrochemical parameters of DSSCs fabricated with 6 μm thick organized mesoporous TiO_2 films and low M_w polymer electrolytes (PEGDME/ SiO_2 /MPII/ I_2) determined from EIS analysis at 100 mW/cm^2 .

| | R_s/Ω | R_1/Ω | R_2/Ω | W_s/Ω | $\omega_{\text{min}}/\text{Hz}$ | τ_r/ms |
|------------|--------------|--------------|--------------|--------------|---------------------------------|--------------------|
| meso1 | 17.7 | 27.2 | 44.8 | 4.3 | 18.7 | 53.5 |
| meso2 | 17.3 | 26.9 | 46.9 | 5.9 | 18.7 | 53.5 |
| meso3 | 17.8 | 27.4 | 36.8 | 7.6 | 10.3 | 97.1 |
| commercial | 17.6 | 30.1 | 48.6 | 13.7 | 25.1 | 39.8 |

The impedance spectra of Fig. S4(a) were interpreted and modeled using equivalent circuits, with each component explained below. Each equivalent circuit consisted of several components: ohmic resistance (R_s), charge transfer resistance at the counterelectrode/electrolyte (R_1), charge transfer resistance at the photoelectrode/electrolyte (R_2), resistance at the Warburg diffusion of the redox I^-/I_3^- couple in electrolyte (W_s). In Fig. S4(a), the Nyquist spectra of the DSSCs showed three semicircles: the first semicircle, in the high-frequency region, represents R_1 ; the second semicircle, in the middle-frequency region, represents R_2 ; the third semicircle, in the low-frequency region, represents W_s , and the curve from the origin to first semicircle starting point on the left represents R_s .

As seen in Table S4, R_s of the DSSCs were not significantly different among the systems because of the same FTO glass resistance. Upon using the organized TiO_2 films, however, other resistances were decreased compared to the commercial TiO_2 film. It indicates a decrease in charge transfer resistance at the FTO/ TiO_2 layer, photoelectrode/electrolyte and the resistance related to Warburg diffusion of the redox I^-/I_3^- couple in the electrolyte. In particular, meso3 showed the lowest R_2 value, which is due to well-developed mesoporous structure with reduced aggregation of P25 nanoparticles and thus improved electron transport in the photoelectrode.

According to the EIS model, the lifetime of electrons for recombination (τ_r) in the TiO_2 photoelectrode can be estimated from the minimum angular frequency (ω_{min}) value of the impedance semicircle at middle frequencies in the Bode spectrum, according to the relationship: $\tau_r = 1/\omega_{\text{min}}$. As seen in Fig. S4(b), the middle frequencies in the Bode spectra of DSSCs shifted to lower frequencies upon using the organized TiO_2 film, and thus

corresponding electron recombination lifetime values (τ_r) for DSSCs increased from 39.8 to 97.1 ms for meso3. A significant increase in the τ_r value indicates the retarded recombination of electron and effective electron transport due to the organized mesoporous TiO₂ layer with good connectivity.