Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Structure Control of Organized Mesoporous TiO_2 Films Templated by Graft Copolymers for Dye-Sensitized Solar Cells

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Experimental Section

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), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA,99%), and copper(I) chloride (CuCl, 99%) were purchased from Aldrich. All chemicals were reagent grade and were used as received.

Synthesis of the graft copolymer

PVC (6 g) was dissolved in 50 mL of NMP by stirring at 90 ^{o}C for 4 h. After cooling the solution to room temperature, various amounts (9 g, 15 g, and 18 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 purged with nitrogen for 30 min. The reaction was carried out at 90 ^{o}C for 18 h. After polymerization, the resultant mixtures were diluted with THF. After passing the solutions through a column with activated Al_2O_3 to remove the catalyst, the solutions were precipitated into methanol. The grafted copolymers were purified by dissolving THF and reprecipitating into methanol three times. PVC-*g*-POEM graft copolymers of three compositions (PVC:POEM=7:3, 4:6,

and 3:7) were obtained in a powder form and dried in a vacuum oven overnight at room temperature.

Preparation of the mesoporous TiO_2 films

A solution was prepared by the slow addition of 0.28 g of HCl (37%) to 0.48 g of TTIP in THF under vigorous stirring. Separately, 0.1 g of amphiphilic PVC-g-POEM graft copolymer was dissolved in 2.9 g of THF and added to the TTIP/HCl/THF solution. This solution was aged by stirring at ambient temperature for at least 3 h. The films were deposited onto a glass slide or FTO conducting glass using a SMSS Delta 80BM spin coater (1500 rpm, 30 sec). Upon calcination at 450 ^{o}C for 4 h, the organic chemicals were completely removed from the mesoporous TiO_2 films.

Characterization

^{1}H NMR measurements were performed with a 600 MHz, high resolution NMR spectrometer (AVANCE 600 MHz FT NMR, Germany, Bruker). XRD measurements were carried out on a Rigaku RINT2000 wide-angle goniometer with a Cu cathode operated at 40 kV and 300 mA. UV-visible spectroscopy was performed with a spectrophotometer (Shimazu) in the range of 200 to 800 nm. TEM images were

obtained from a JEOL JEM 1010 microscope operating at 300 kV. For the TEM measurements, the graft copolymers were first dissolved in THF. A drop of this solution was then placed onto a standard copper grid. Morphologies of the mesoporous TiO_2 films were observed using a field-emission scanning electron microscope (FE-SEM, SUPRA 55VP, Germany, Carl Zeiss).

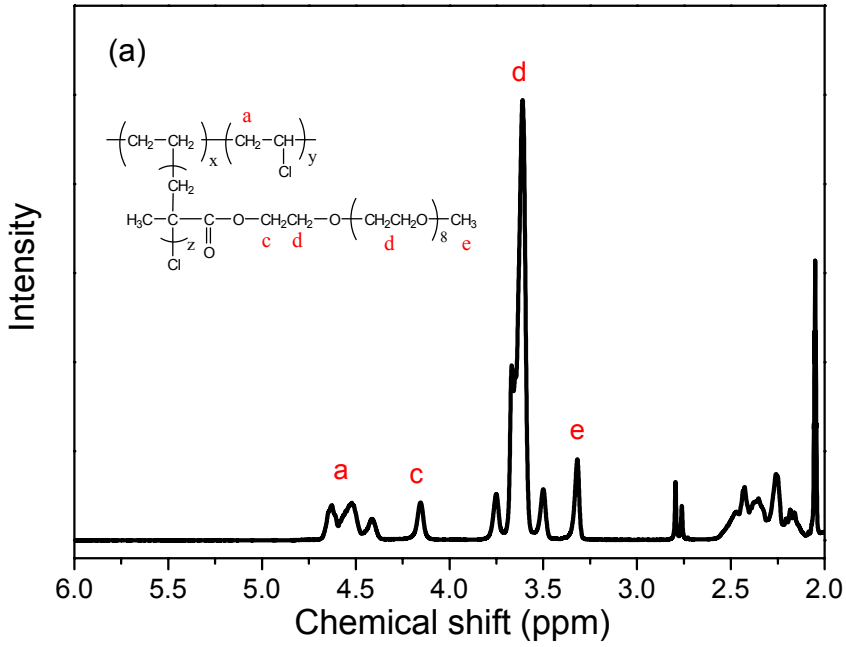
Fabrication of the DSSCs

DSSCs with an active area of 0.16 cm^2 were fabricated according to a previously reported procedure.[18-20] Transparent SnO_2/F-layered conductive glass (FTO, Pilkington. Co. Ltd., 8 Ω/□) was employed in order to prepare both the photo and counter electrodes. For the photoelectrode, a Ti(IV) bis(ethyl acetoacetato) diisopropoxide solution (2% w/w in 1-butanol, Aldrich) was first spin-coated onto the FTO glass. The glass was then heated stepwise to 450^oC and maintained at this temperature for 20 min. The sol-gel solutions were then spin-coated onto the FTO glass and sintered at 450 ^oC for 30 min. The nanocrystalline TiO_2 mesoporous films were sensitized overnight in a $Ru(dcbpy)_2(NCS)_2$ dye (dcbpy = 2,2□-bipyridyl-4,4□-dicarboxylato) solution (535-bisTBA, N719, Solaronix, 13 mg dissolved in distilled ethanol (50 g)). Pt-layered counter-electrodes were prepared by spin-coating a 1 wt%

H_2PtCl_6 solution in isopropanol onto the FTO glass and then sintering the film at 400 □C for 30 min. Polymer electrolyte solutions consisting of PVC-g-POEM graft copolymer, 1-methyl-3-propylimidazolium iodide (MPII), and I_2 (10 wt% of MPII) dissolved in THF were cast onto a dye-adsorbed TiO_2 electrode and evaporated very slowly to allow penetration of the electrolytes through the mesopores of the TiO_2 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.

The photoelectrochemical performance, including the short-circuit current (J_{sc}, mA/cm^2), 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 (Oriel, 91193). The light was homogeneous up to an 8 × 8 in^2 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/cm^2). The intensity was verified with a NREL-calibrated Si solar cell (PV Measurements Inc.).

Figure S1. ^{1}H NMR spectra of the PVC-g-POEM graft copolymer; (a) PVC:POEM=7:3 and (b) PVC:POEM=3:7 wt%.



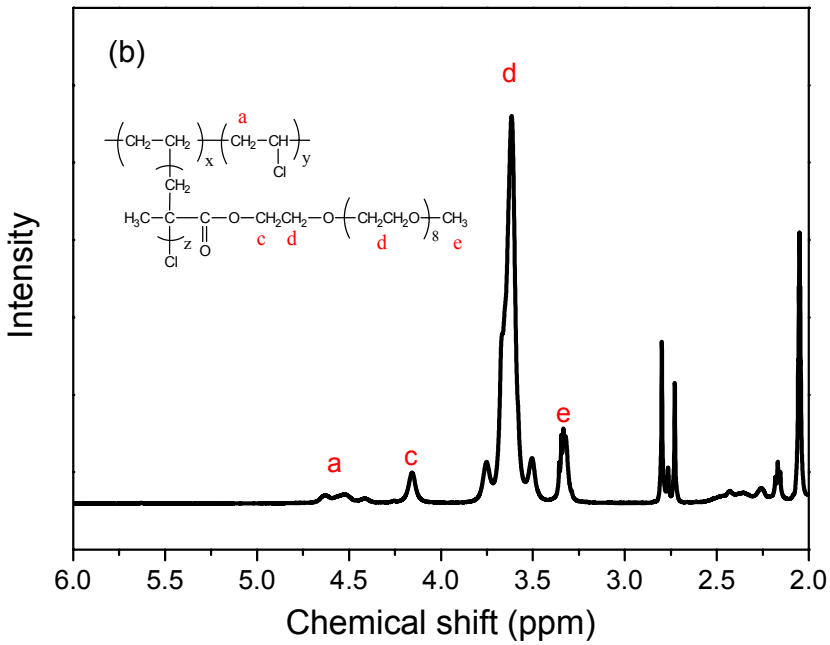


Figure S2. TEM images for PVC:POEM=4:6; (a) graft copolymer prepared from THF, (b) large-scale view of the graft copolymer prepared from THF/H_2O/HCl, (c) graft copolymer prepared from THF/H_2O/HCl and (d) mesoporous TiO_2 films templated by the graft copolymer.

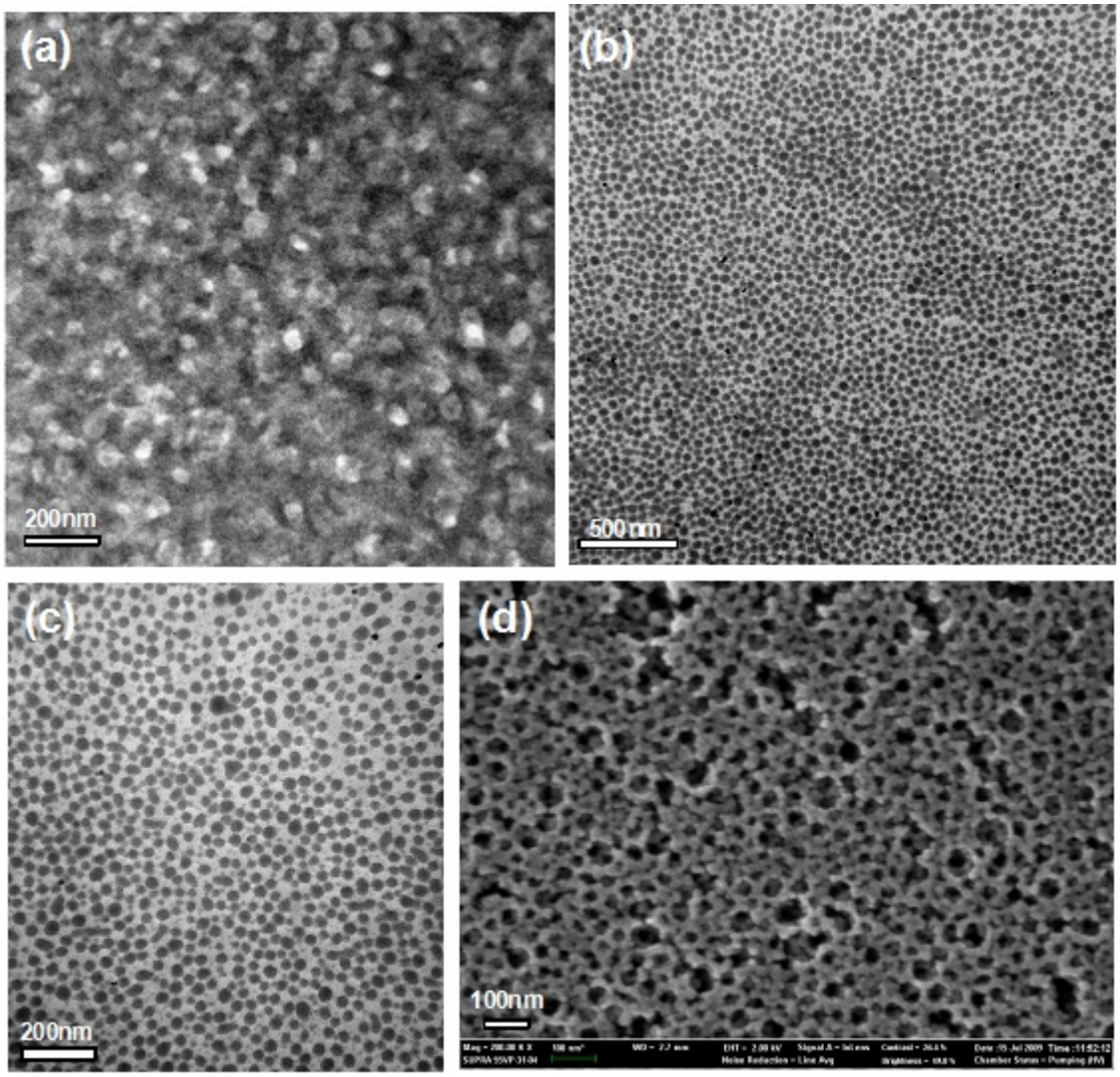


Figure S3. XRD patterns of mesoporous TiO_2 films templated by the graft copolymer.

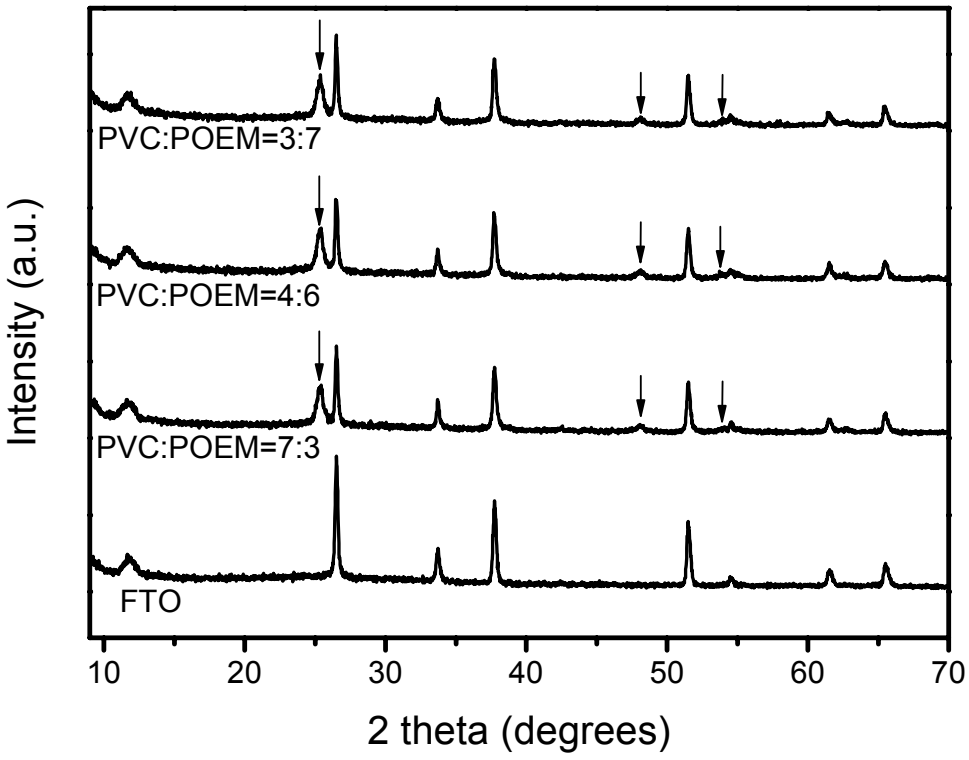


Figure S4. UV-visible spectra of mesoporous TiO_2 films templated by the graft copolymer.

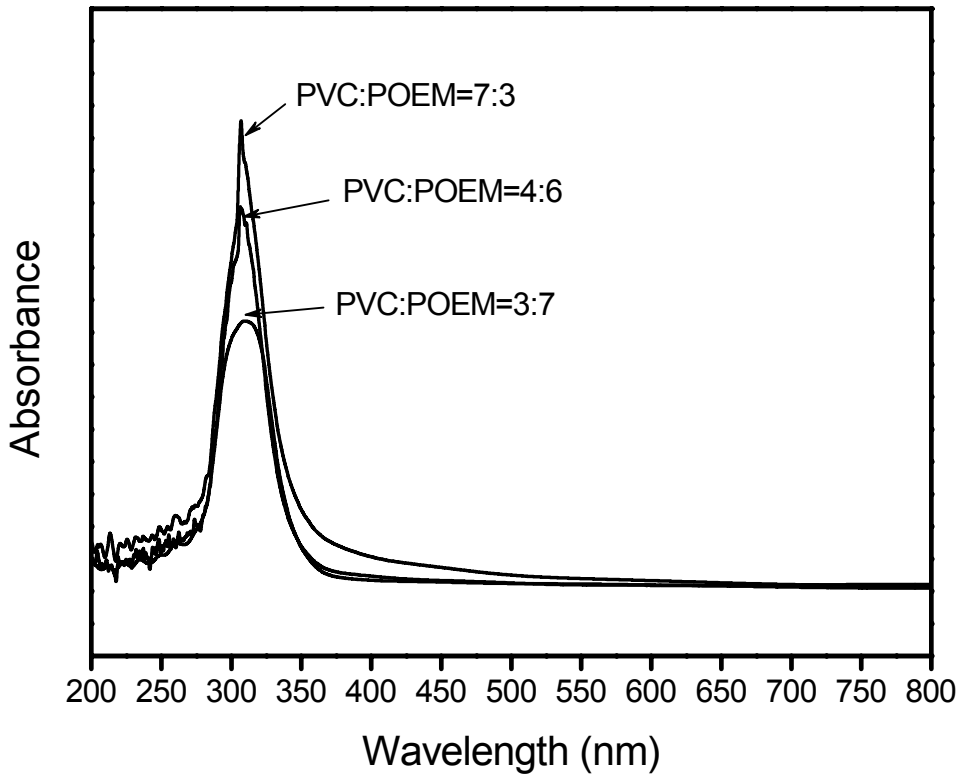


Figure S5. SEM image for randomly oriented TiO_2 film prepared by commercial paste (Ti-Nanoxide D20, Solaronix).

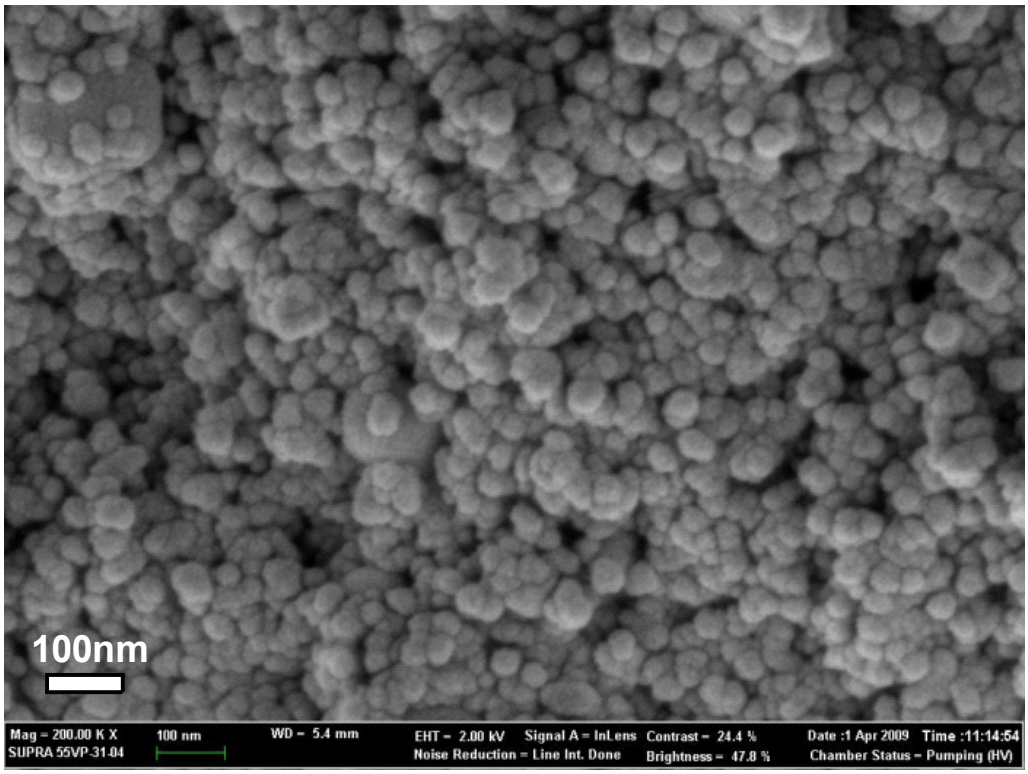


Figure S6. J-V curves for DSSCs fabricated using multilayer mesoporous TiO_2 films (2.5 μm thickness) templated by the PVC-g-POEM (3:7) graft copolymer and PVC-g-POEM/MPII/I_2 electrolytes.

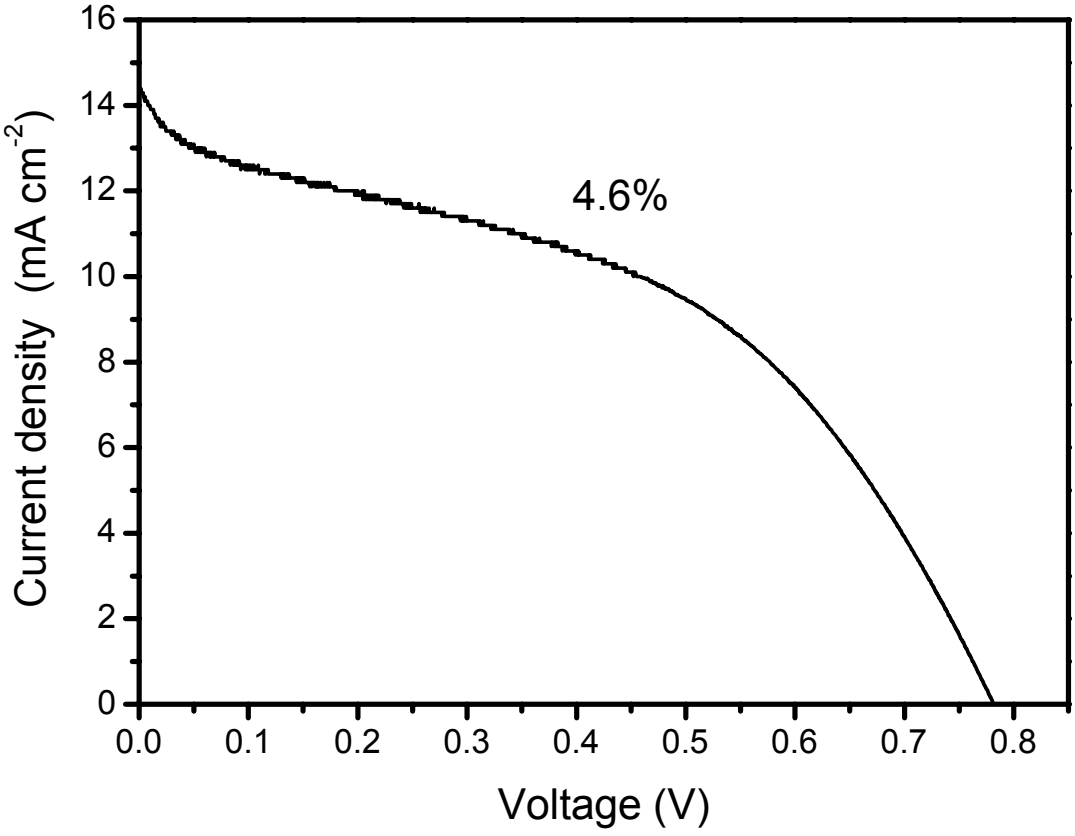


Figure S7. SEM images for five-layer TiO_2 film (a) surface and (b) cross-section.