Supporting Information

Dye-Sensitized Solar Cells Based on Hierarchically Structured Porous $\rm TiO_2$ Filled with Nanoparticles

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Figure S1. SEM images of PMMA-*y* (*y* represents the diameter of PMMA micro-sphere) and the 3DOM_TiO₂-*x* samples (x = 155 nm (c), 115 nm (f), 105 nm (j), and 85 nm (l)), copied by the corresponding PMMA-280 (a, b), PMMA-220 (d, e), PMMA-200 (g, h), and PMMA-150 (j, k) micro-spheres, respectively.



Figure S2. (A) N_2 adsorption-desorption isotherms at 77 K and (B) pore-size distributions calculated by the Barrett-Joyner-Halenda (BJH) method and (C) N_2 adsorption isotherms at low-pressure section of (a) Ti-155, (b) Ti-115, (c) Ti-105, and (d) Ti-85 samples.



Figure S3. TGA/DSC profiles of the representative Ti-105 sample after drying without calcination at high temperatures.

Figure S3 shows the TGA/DSC profiles of the Ti-105 sample before calcination at high temperatures. It is found that a gradual small weight loss of 10 wt% happened below 180 °C accompanying by the appearance of a exothermal signal at 140 °C, ascriable to the remove of adsorbed water form atomsphere; there were a weight losses of 17 wt% in the 180 – 320 °C and another obvious one of 62 wt% in the range of 320 - 430 wt%. Their correspoding endothermic signals at 250 °C and 380 °C, assignable to the decomposition of Ti precursor and the elimination of the template PMMA and the surfactant PEG. There is no further weight loss above 500 °C indicating that the calcination temperature 550 °C is appropriate for the formation of single crystal-phase TiO₂ crystallinites.

F =	- <u>_</u> - <u>_</u> - <u>_</u>			
Sample	BET surface area	Pore diameter ^b	Pore volume ^b	surface area/
	$(m^2/g)^a$	(nm)	(cm^{3}/g)	Pore volume (cm ⁻¹)
Ti-155	46.1	24.6	0.25	184
Ti-115	60.4	23.5	0.33	183
Ti-105	72.2	22.5	0.52	138
Ti-85	114.5	25.6	0.82	140

Table S1. Textural parameters of the as-prepared three-dimensional ordered hierarchical-porous TiO_2 samples

^a calculated according to BET method, ^b calculated according to BJH method.