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A one-pot solvothermal strategy for hierarchical microspheres with radially assembled single-crystalline TiO_2-nanorods as high performance photoanode materials in dye-sensitized solar cells

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Experimental section

3 ml of 12% $TiCl_3$ acidic aqueous solution (Sigma-Aldrich, #14010) diluted with 3 ml of DI water were added into a Teflon-lined autoclave of 18 ml capacity, followed by addition of 6 ml of *n*-butanol (Merck, S5589462). Subsequently, the autoclave was sealed and placed in an oven at desired reaction temperature for 4h. After natural cooling to room temperature, the product was washed using DI water and ethanol for 3 times and dried in air. The reaction temperature was controlled at 110, 130, 150, 170 and 190 °C, respectively. The obtained serial samples were labelled with the corresponding reaction temperature. For instance, the sample prepared at 150 °C was labelled as T150. A control sample of T150 was synthesized at 150 °C but without the addition of *n*-butanol. The electrodes were fabricated via the doctor-blade technique using the above materials and P25 (Degussa) on fluorine-doped tin oxide (FTO) glass and calcined at 500 °C in air for 30 min. The thickness and active area of the electrode films were controlled at ~ 9 μm and 0.2 cm^2, respectively. The as-prepared electrodes were sensitized by immersing in ethanol solution, containing 0.4 mM N719 dye (Solaronix) for 20 h. These sensitized photoanodes were sandwiched with platinum-coated FTO counter electrodes and sealed using a ~ 35 μm thick polypropylene spacer between two electrodes. The liquid iodide electrolyte (Iodolyte AN-50, Solaronix) was injected into the internal space of cells through reserved channels, which were also sealed after injections.

The morphology of the hierarchical microspheres was observed using transmission electron microscopy (TEM, JEOL-2010 microscopes) at 200 kV and field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). The particle size distribution was evaluated by a particle size analyzer (90Plus, Brookhaven Instruments Corporation).The phases of the TiO_2 were identified by X-ray diffraction (XRD) analysis using Bruker D8 X-ray diffractometer with Cu Kα radiation as the X-ray source (λ = 1.5406 Å). The UV-Vis DRS of the obtained powders were recorded on a UV-Vis spectrophotometer (UV-Vis, Varian Cary 5000). The specific surface area of the sample powders was measured with a commercial surface area analyzer (Quantachrome Adsorb-1) and calculated using the Brunauer-Emmett-Teller (BET) equation. The *J*-V characteristics of DSSCs with different electrodes were measured by an electrochemical analyzer (Keithley 2420 SourceMeter) under solar simulator illumination (ABET Technologies Sun 2000 Solar Simulator, 100mW cm^{-2}, AM 1.5G spectrum). The IPCE evaluation were conducted using Newport lamp (100mW cm^{-2}) and light filters as monochromatic light source, with a Si photovoltaic cell as reference. The EIS were performed using PARSTAT 2273 Advanced Electrochemical system (Princeton Applied Research) with frequency range from 0.1 Hz to 100 kHz at an applied bias of V_{oc} under the illumination of one sun.

Supplementary results

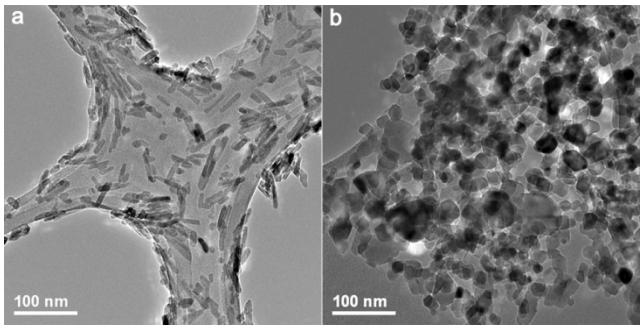

Fig. S1 TEM images of T150B- (a) and P25 (b).

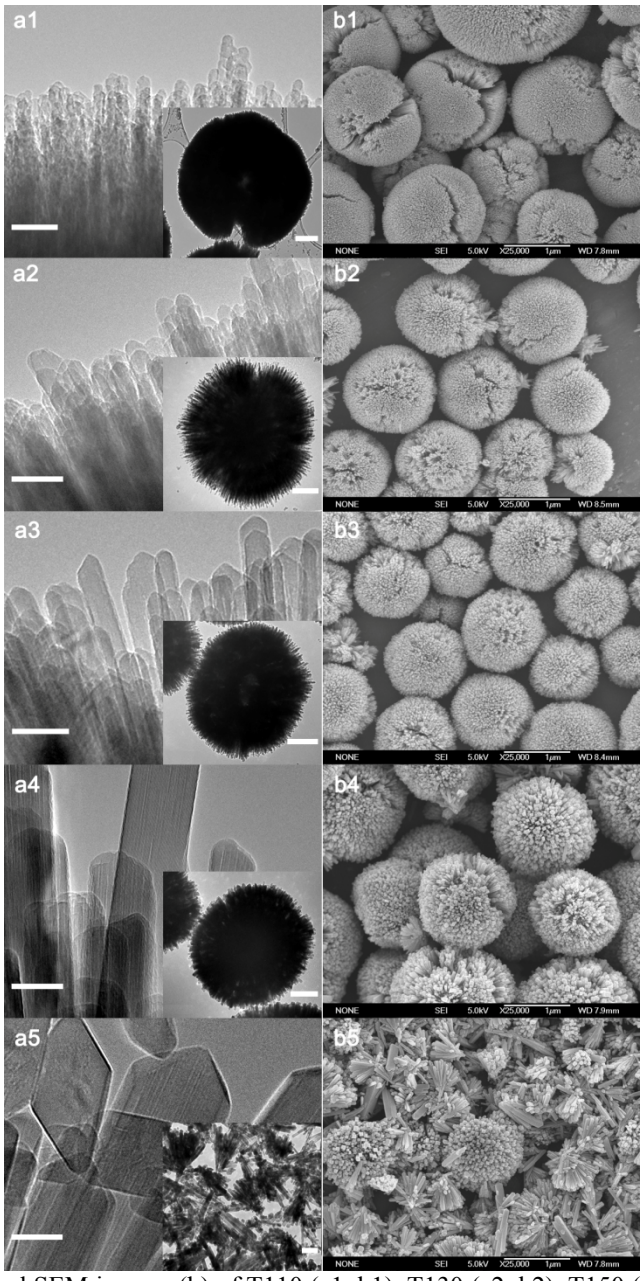

Fig. S2 TEM images (a) and SEM images (b) of T110 (a1, b1), T130 (a2, b2), T150 (a3, b3), T170 (a4, b4) and T190 (a5, b5). The scale bars in (a) and the insets of (a) are 20 nm and 0.2 μm, respectively.

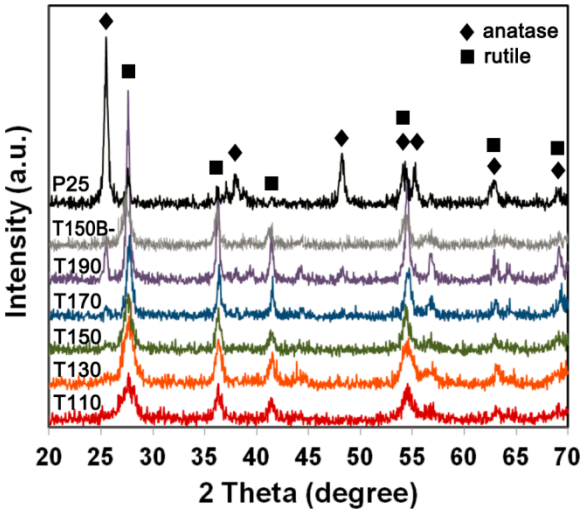

Fig. S3 XRD patterns of the five microspheres, P25 and T150B- powders.

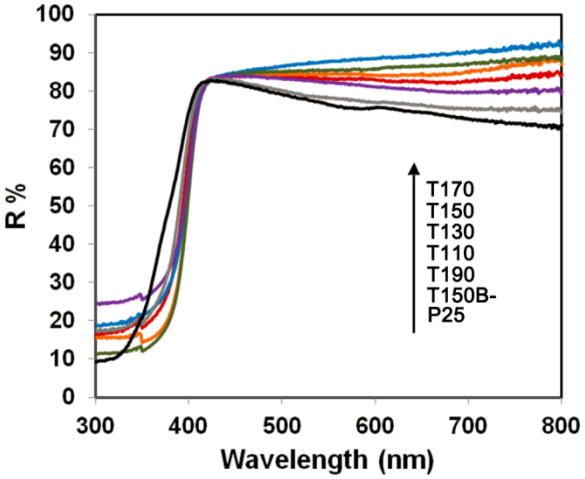

Fig. S4 UV-Vis DRS of the five microspheres, P25 and T150B- powders.

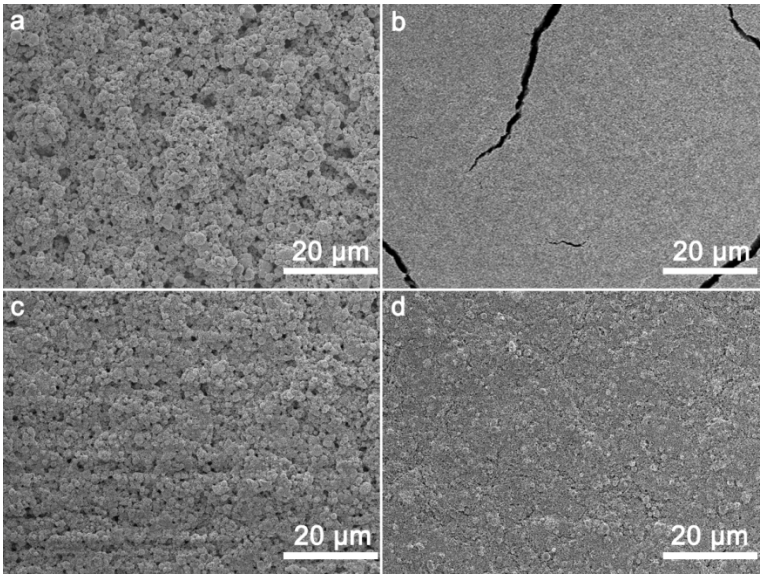

Fig. S5 SEM images of the electrode films prepared using T150 (a), P25 (b) and a mixture of weight ratio of T150 and P25 at 80:20 (c) and 60:40 (d).

Table S1 Morphology parameters of the hierarchical microspheres, T150B- and P25 powders

Sample	Average particle size (nm)	Average Rod diameter (nm)	S_{BET} ($m^2 g^{-1}$)
T110	1032	7	84.69
T130	925	10	97.07
T150	831	14	89.24
T170	853	21	63.68
T190	463	30	49.28
T150B-	45*	14	97.54
P25	27	--	58.18

* Average length of the nanorods.

Table S2 Performance parameters of all DSSCs

Sample	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
T110	8.89	0.745	61.5	4.09
T130	9.48	0.762	65.9	4.74
T150	9.32	0.788	66.7	4.90
T170	7.91	0.771	66.1	4.05
T190	7.36	0.771	62.0	3.50
T150B-	7.66	0.745	65.7	3.75
P25	8.31	0.753	64.9	4.06