Supplementary Information

An over 10% enhancement on dye-sensitized solar cell efficiency by tuning nanoparticle packing

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Experimental

Crystalline TiO_2 nanoparticle aggregates. The highly crystalline TiO_2 nanoparticle aggregates were synthesized as reported previously. Precursor were prepared by mixing a solution comprising 0.1 M titanium butoxide in acetonitrile/buta-1-ol (with a volume proportion of 1:1) and another 1:1 acetonitrile/butan-1-ol (V/V) solution containing 0.1 M water and 0.2 M ammonia (28%, Ajex Fine Chemical) under constant stir. Precipitate, aged approximately 2 hours, was washed with ethanol and collected by centrifuge. Crystalline mesoporous TiO_2 nanoparticle aggreates were prepared by redispersing the precursor spheres into water/ethanol mixture (with a volume proportion of 1:1) with 0.5 mL ammonia and hydrothermally treated at 150 ^oC for 15 hours. The products were collected from Teflon lined autoclave, washed with ethanol and dried at room temperature.

Dye-sensitized solar cell construction. The highly crystalline mesoporous TiO_2 spheres (sample HA, 2.5 g) was dispersed in absolute ethanol (50 ml) and sonicated for 30 min. Ethyl cellulose (1.25 g) and terpinol (10.0 g) were added to the solution and finely dispersed by sonication and stirring before evaporated at 40 ^oC to a paste. A thin blocking layer of TiO_2 were prepared on FTO glass (Nippon, 10 Ω/square) by spray pyrolysis of 7.5% w/w solution of titanium isopropoxide bisacetylacetonate in ethanol at 450 ^oC. Photoanode films (4×4 mm^2) were printed onto FTO glass by using a screen printer and dried at 125 ^oC between each printed layer to obtain a variety of film thicknesses. The films were compressed at 150 Mpa for 3 mins by using a commercialized isostatic pressing (CIP) equipment before sintered in air as follows: 150 ^{o}C for 10 min, 325 ^{o}C for 5 min, 375 ^{o}C for 5 min, 450 ^{o}C for 30 min, and finally 500 ^{o}C for 15 min. These films were subsequently treated with a 40 mM aqueous $TiCl_4$ solution at 70 ^{o}C for 30 min and re-sintered for 30 min at 450 ^{o}C before sensitized in a 0.3mm N719 solution overnight.

Counter electrode were prepared by thermally decomposing H_2PtCl_6 (10 mM in ethanol) on FTO glass. Sandwich cells were assembled by sealing the photoanode onto the Pt counter electrode with a 25 μm thick Surlyn (8×8 mm^2). The electrolyte, containing 0.03 M iodine, 0.5 M 4-terbutylpyridine, 0.6 M 1-butyl-3-methylimidazolium iodide, and 0.1 M guanidinium thiocyanate in a mixed acetonitrile/valeronitrile (V/V = 17 : 3) solution, was introduced into the cell via a vacuum filling method.

Characterization. The thickness of the electrode films was measured by using a profilometer (DEKTAK 150, Veeco Instruments Inc). Morphologies of the photoanode films before and after high pressure compressing process were observed by using a high resolution field emission scanning electron microscope (SEM, JOEL 7001F). Nitrogen adsorption – desorption isotherms were measured on a Micromeritics Tristar 3000 system. Specific surface areas were measured by degasing samples at 150 ^{o}C on a vacuum line and calculated by utilizing a standard Brunauer-Emmett-Teller (BET) method. Dye uploading capacities were measured by detaching dye molecular from sensitized photoanode films.

The sealed solar cells were shielded by a black metal mask with an aperture area of 6×6 mm^2, and measured the photovoltaic properties using a Keithley 2400 Source Meter under the irradiation of simulated sunlight (100 mW/cm^2) provided by an Oriel solar simulator with an AM 1.5 filter. IPCE plotted as a function of excitation wavelength was recorded on a Keithley 2400 Source Meter under the irradiation of a 300 W xenon lamp with an Oriel Cornerstone^{TM} 2601/4m monochromator. Electrochemical impedance spectra (EIS), measured with an AutoLab PST A30 in a frequency range of 0.1 – 10^5 Hz under dark with an applied electrical bias dropping from the 900 mV to 500 mV with a 50 mV interval, were fitted in Zview software with a transmission line model. DSC EIS spectrum generally comprises three distinctive parts associated with electrochemical processes of different time domains, i.e. the fast response from charge transfer at counter electrode in the high frequency domain, the signal from carrier transport and recombination in the semiconductor layer in the mid-frequency domain and the slow response from the Nerstain diffusion of redox couple species in the electrolyte taking place in the low frequency domain. Depending on the characteristic time constants of the individual processes, responses from one or more processes would dominate the EIS spectrum and provide pertinent information of the whole device. Calculated capacitance (diode model) plotted against V_F and conduction band positions (V_{ecb}) can be found in Figure S-3.

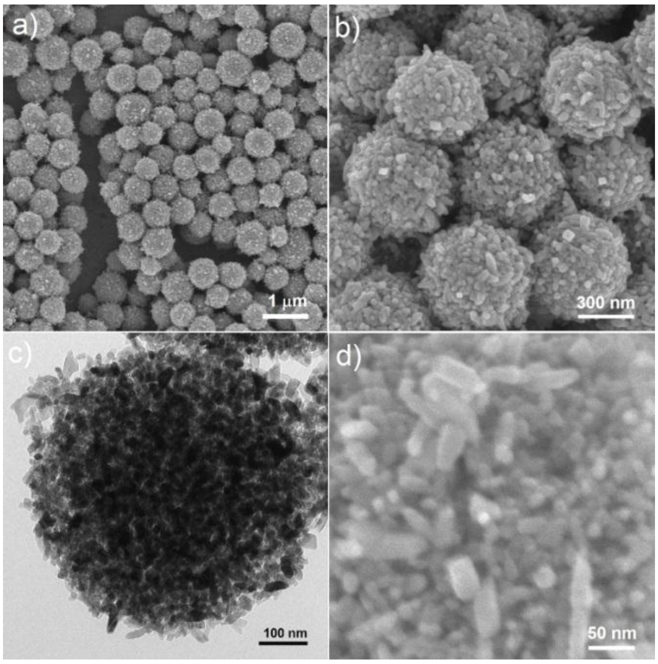

Figure S-1. SEM and TEM images of spherical crystalline TiO_2 nanoparticle aggregates (HA) [5].

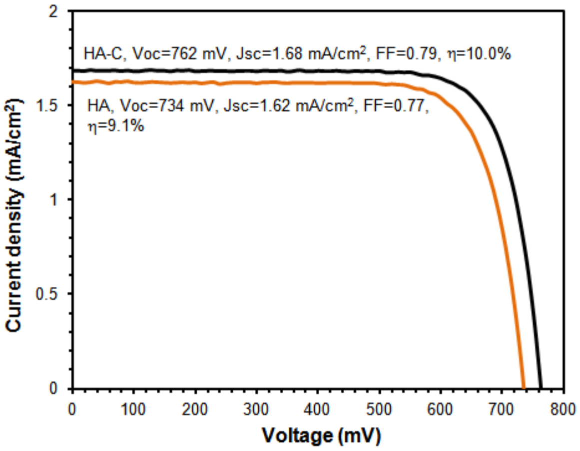

Figure S-2. I-V curves of sensitized HA photoanodes a) before and b) after compression at 10% of AM 1.5 simulated sunlights, measured with a 6×6 mm^2 mask.

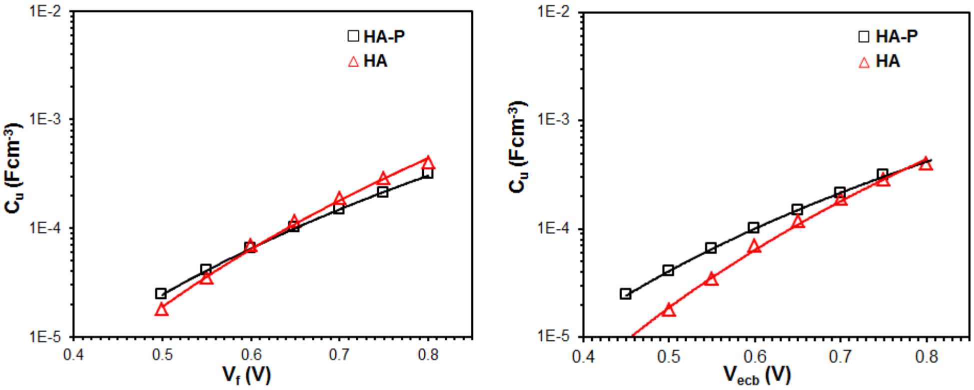

Figure S-3. Calculated capacitance (diode model) plotted against Fermi level voltage (V_F) and common equivalent conduction band positions (V_{ecb}). For the electrode prepared from the same materials, such as HA TiO_2, the compressing treatment would not change the chemical properties of the electrode materials, resulting in the almost unchanged trap distribution and bend edge of HA TiO_2. This can be observed from the above figure as δ_{Ec} is close to 0.05. [6 c)]

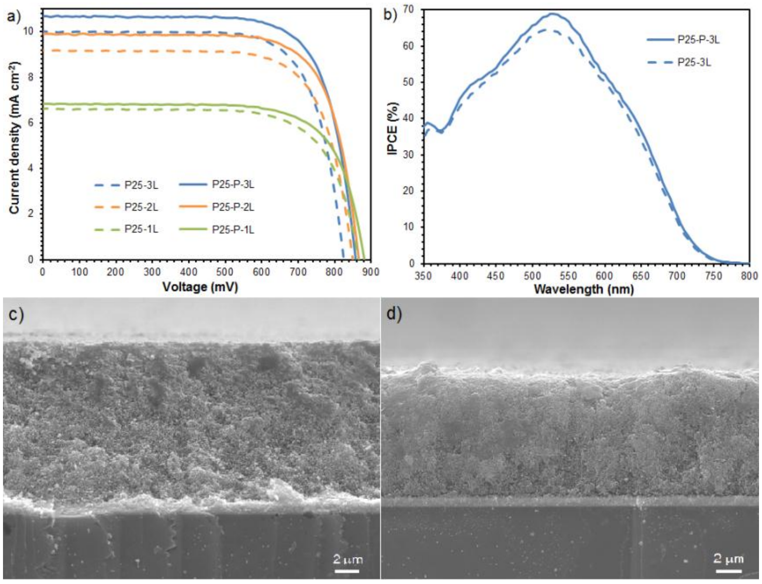

Figure S-4. (a) I-V curves of the sensitized photoanodes prepared from P25 nanoparticles with varying film thickness and (b) corresponding IPCE curves of the sensitized 3L P25 TiO_2 photoanode film before and after compressing. Film thickness: 1L, 6 µm; 2L, 12 µm; 3L 18 µm. SEM cross section images of P25 photoanode film (c) before and (d) after compressing. The dye loading capacities are of 38 nmol/g vs 35 nmol/g for P25 photoanode films before and after compressing.

Table S-1. Photovoltaic performances recorded at AM 1.5 simulated sunlight for the sensitized P25 photoanodes before and after compressing, measured with a 6×6 mm^2 mask, average from 8 electrodes for each film thickness.

Film thickness before press	P25				Film thickness after press	P25-P			
	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η (%)		V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η (%)
6 μm	866	6.6	0.71	4.1	5 μm	881	6.8	0.72	4.4
12 μm	850	9.2	0.73	5.7	10 μm	866	9.9	0.73	6.3
18 μm	825	10.0	0.73	6.0	15 μm	858	10.7	0.74	6.7

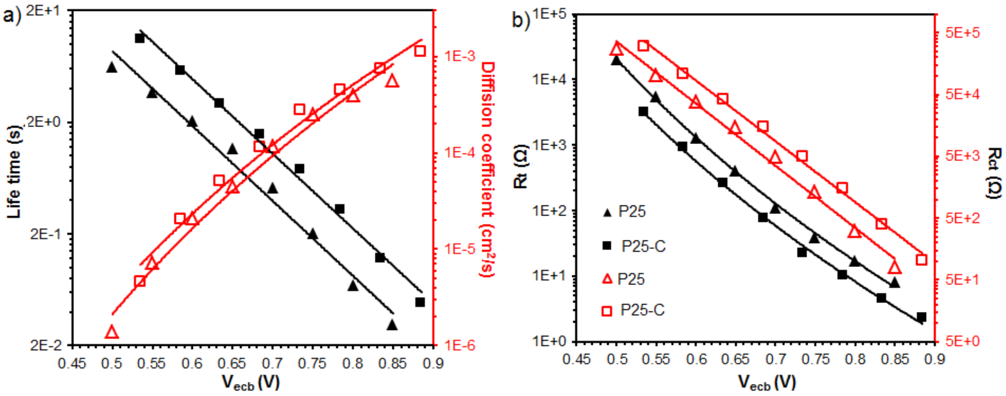

Figure S-5. a) Electron life time (τ_n) and diffusion coefficient (D_n), and b) electron transfer resistance (R_t) and recombination resistance (R_{ct}) of sensitized P25 photoanodes before and after compressing, as a function of common equivalent conduction band positions (V_{ecb}).