Supporting information

The effect of amorphous TiO_2 in P25 on Dye-Sensitized Solar Cell performance

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S1 -Experimental Methods

S1.1 Synthesis of modified P25 nanoparticles

P25 (supplied by Nippon Aerosil), tetra propylammonium hydroxide (TPA, ca. 40% in water, purchased from Tokyo Chemical Industry Co., Ltd.), water and ammonium fluoride (NH_4F, purchased from Kanto Chemical Co., Inc.) were mixed at a molar ratio of P25:TPA:H_2O:NH_4F = 1:0.8:5:0.2 in a Teflon-lined stainless-steel autoclave and the mixture treated at 443 K for seven days. The product was recovered by centrifugation and repeatedly washed with water.

S1.2 Preparation of H-P25 and P25 photoanodes and DSC assembly

H-P25 and P25 photoanodes were prepared as follows: pastes of each material was made by grinding 1 g of either treated or untreated P25 powder rigorously with (25 ml) absolute ethanol, (1 ml) distilled water, (0.2 ml) acetic acid. After that, 5 g of a binder solution (10 wt% ethyl cellulose in ethanol) and 5 g terpinol were added to the mixture. The formed slurry was stirred and then sonicated for an hour. Following this, the ethanol, water, and acetic acid were evaporated using a rotary evaporator.

FTO glass was sonicated three times (20 minutes) in each of soapy water, acetone, and ethanol. A dense TiO_2 blocking layer was deposited on FTO substrate by spray pyrolysis of a solution of diluted titanium diisopropoxide bis (acetylacetonate) (75% in isopropanol) (Aldrich), in absolute ethanol (1:9 v/v). To form the mesoporous structure of photoanodes, H-P25 and P25 pastes were cast in thickness (11.5 ± 0.3 μm) using a Dr Blade method on pre-cleaned FTO glass. The deposited photoanodes were sintered using sequential annealing process to remove organic components. After cooling down to 110 °C, photoanodes were sensitized with a commercial organometallic dye (N719 Solaronix), by immersion in a 0.5 mM dye bath using a mixture of solvents (1:1) acetonitrile (HPLC, Lab-scan):tert-butanol (LR, Ajax Chemicals). After 24 hours dying time, the films were rinsed with acetonitrile and dried. Another a piece of FTO glass, with a Ø=1 mm port, was coated with a drop of (10 mM) platinic acid solution (H_2PtCl_6) in ethanol which was thermally decomposed by heating at 400 °C for 20 min to form the counter electrode. Sensitized working electrode and platinum counter electrode were sealed together using a spacer of 25 µm Surlyn (Solaronix) by a hot-press. A liquid electrolyte consisting of acetonitrile and valeronitrile [85:15 vol%] with 30 mM iodine (I_2), 0.5 M 4 tertbutyl pyridine (4-tBP), 0.6M 1-butyl-3-methylimidazolium iodide (BMII) and 0.1 M guanidinium thiocyanate (GuSCN)] was introduced between the sealed working and counter electrodes using a vacuum back-filling technique. Finally, a piece of Aluminum foil backed Surlyn was used to seal counter electrode port.

S1.3 Characterizations

X-ray diffraction patterns of the crystalline structure of treated and untreated P25 were examined by using RIGAKU Smart Lab in range (20° - 40°) using 1°/min scan speed. The surface morphologies and internal structure were obtained transmittance electron microscopy (JEOL JEM-6500F). Brunauner-Emmet-Teller (BET) measurements including specific surface area and adsorption-desorption data, were conducted using (MicrotracBel Belsorp-mini). Optical properties of photoanodes including (absorption, transmittance, the diffuse reflection was obtained using Ultraviolet-Visible-NIR light spectroscopy (Shimadzu UV-3600) with an integrating sphere attachment. Dye-sensitized H-P25 and P25 photoanodes immersed for (5 minutes) into a (0.1 M) NaOH solution (mixed solvent water and ethanol 1:1 v/v) and the amount of desorbed dye molecules was quantified by measuring the absorption spectrum of desorbed dye solution (on three films for each) by photospectroscopy (Shimadzu UV-1800). Film thicknesses were measured using a Surface Profiler (Veeco Dektak 150). Photocurrent density-voltage (J-V) was measured using a PV Measurements (Colorado) solar simulator with AM1.5 filter; set to 1 sun (100 mW/cm^2). A QEX10 system, also from PV

Measurements, was used for Incident Photon to charge carrier Conversion Efficiency (IPCE) measurements. Electrochemical impedance spectroscopy (EIS) including Nyquist and Bode plots was measured using a Reference 600 Potential/Galvanostat/ZRA (GAMRY INSTRUMENTS) under 1 sun illumination and at V_{oc} in the frequency range of 0.1 - 10^6 Hz using 10 mV perturbation.

Devices	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
P25_1	7.2	0.78	59	3.4
P25_2	7.3	0.80	58	3.4
P25_3	7.3	0.77	50	2.8
AV	7.3	0.78	56	3.2
STDEV	0.1	0.02	5	0.3
H-P25_1	9.6	0.79	69	5.0
H-P25_2	11.0	0.79	57	5.0
H-P25_3	9.9	0.80	74	6.0
AV	10.2	0.79	67	5.3
STDEV	0.7	0.01	9	0.5

Table S1: J-V parameters of measured DSC devices based H-P25 and P25 photoanodes.

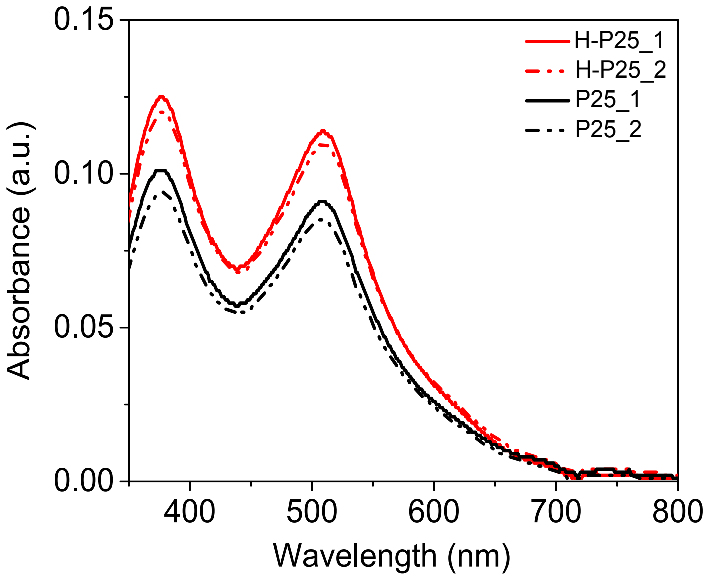

Fig. S1: Absorption spectra of desorbed dye solution of N719 dye-sensitized H-P25 and P25 photoanodes (two films for each).

Table S2: Dye loading measurements of H-P25 and P25 sensitized with N719 dye, (two films for each, thickness=5.5 ±0.25 µm, Area=1 cm^2).

Sample	Moles of dye (nmol)	Amount of dye (nmol/cm^2)	Amount of dye (µmol/cm^3)
P25_1	25	25	49.5
P25_2	23	23	46.3
H-P25_1	31	31	62.0
H-P25_2	30	30	59.9

S2- Optical measurements

Fig. 2Sa shows the light transmitted by the undyed H-P25 photoanode is lower than that of undyed P25 photoanode in the wavelength range of 400-800 nm. This is because H-P25 has slightly less porosity, due to larger agglomeration particles leading to the more dense film which has slightly lower transmittance. Also, the larger pore size in H-P25 (inset Fig. 1e) should enhance longer wavelength scattering. Similarly, the transmittance of dyed H-P25 photoanode is lower than that of the P25 one in the wavelength range 400-800 nm. Fig. 2Sb shows the diffuse reflectance spectrum of H-P25 and P25 photoanodes. Undyed H-P25 photoanode showed slightly higher diffuse reflection in the visible region. As for dyed photoanodes, both photoanodes showed similar diffuse reflection in the wavelength range 400-700 nm with a slight increase in diffuse reflectance of H-P25 in the near infrared range 700-800 nm. Fig. 2Sc shows the absorption of undyed H-P25 photoanode is slightly higher than that of P25 photoanode while after being dyed; the absorption values of dyed H-P25 photoanode are higher than that of dyed P25 photoanode across the entire wavelength range. This means that dyed H-P25 film has higher light harvesting in the entire wavelength range due to owing higher dye loading along with slightly higher diffuse reflection than that of dyed P25. Fig. 2Sd shows higher adsorbed dye on H-P25 photoanode compared to P25 which is in good agreement with dye loading measurements resulting in enhanced photocurrent.

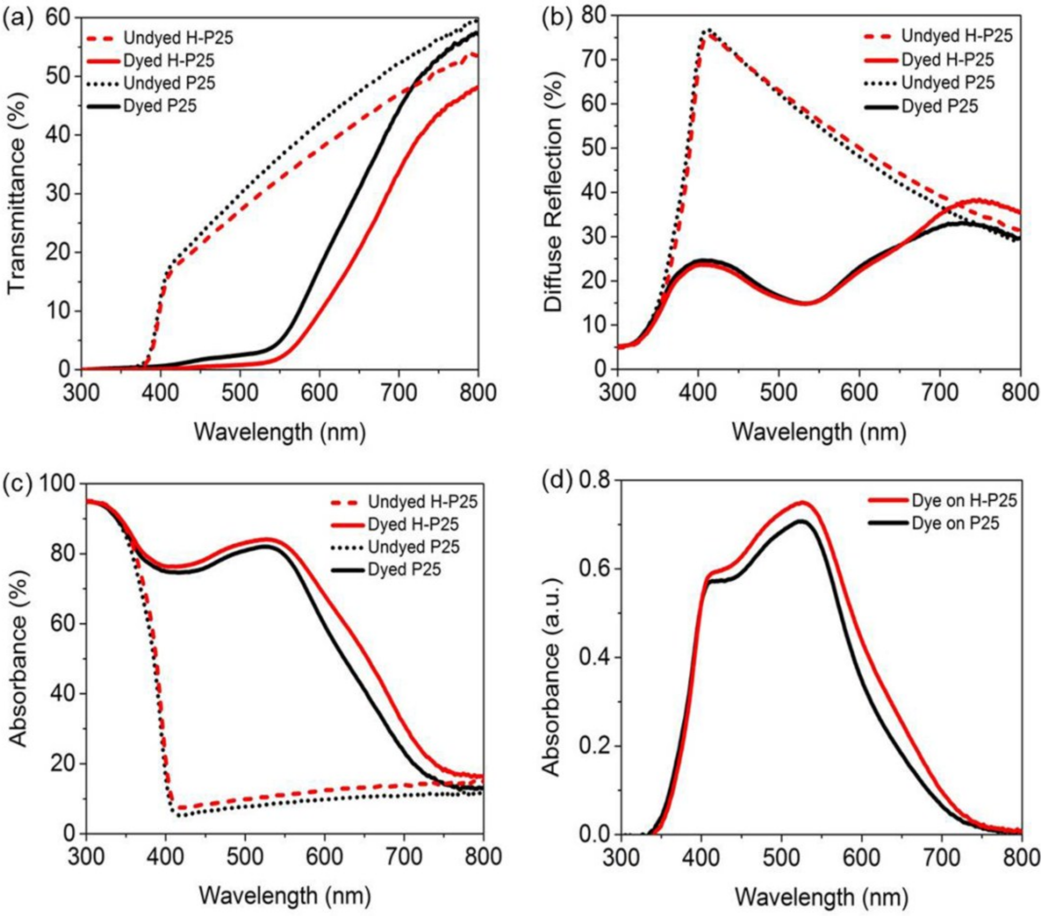

Fig. S2: Optical measurements of H-P25 and P25 photoanodes; (a) Transmittance; (b) Diffuse reflection; (c) Absorbance; (d) Absorbance of dye.

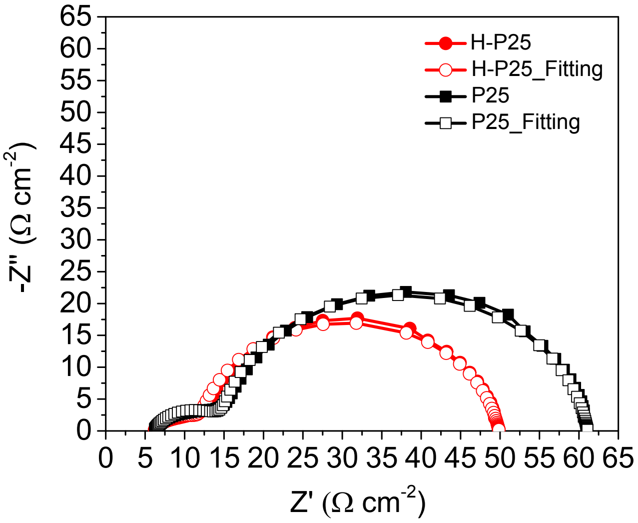

Figure S3: Fitting data of Nyquist plots of DSC devices based on H-P25 and P25 photoanodes sensitized with N719 dye.