

Electron Transport Properties in Dye-sensitized Solar Cells with {001} Facet-Dominant TiO₂ Nanoparticles

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S1 Experimental Details

S1-1. Preparation of TiO₂

S1-1-1 Hydrothermal synthesis of anatase TiO₂

TiO₂ nanoparticles were synthesized under microwave hydrothermal reaction with previously reported procedure¹⁻⁴. The synthesis procedure consists of the precursor solution composed of tetrabutoxytitanium(IV) (Ti(OBu)₄, 25 mL) and aqueous hydrofluoric acid solution (HF, 6 mL, 23 wt%) NS. The mixed precursor solutions were then tightened in a Teflon-lined autoclave container and kept at 200 °C for 35min in a microwave oven (Milestone General, Japan). The white powdery precipitates were washed with ethanol and distilled water several times by a sonication followed by a decantation. The defluorination was carried out by washing samples with aqueous NaOH solution (0.1M) through a decantation a few times in order to remove the fluorinated titanium products on TiO₂ surface¹⁻⁴. Although NP does not contain the fluoride compound, same procedure of washing with NaOH solution was applied for avoiding the unknown effects of NaOH washing on the characteristics. And then, the particles were washed by 0.1M hydrochloric acid aqueous solution a few times, and re-dispersed in the ethanol after decantation with deionized (DI) water reached above pH 7. The ethanoilic suspensions of NP and NS TiO₂ were processed to prepare TiO₂ paste.

S1-1-2 Preparation of anatase TiO₂ Paste

Earned TiO₂ nanoparticle suspensions in ethanol were then processed to prepare a TiO₂ paste for creating mesoporous TiO₂ films by adding binders of α -terpineol and ethylcellulose dispersed in ethanol. The mixed suspensions composed of TiO₂ (2.73 wt%), ethanol (84.8 wt%), α -terpineol (11.1 wt%), ethylcellulose (18-22mPa, 0.77 wt%) and ethylcellulose (45-55mPa, 0.60 wt%) were homogenized under ultrasound sonic-hone (titanium) followed by ball milling with zirconia beads for 20h.⁵ Finally the ethanolic solvent was evaporated by rotary evaporator under 45 °C to earn the 8~10wt% of TiO₂ as the paste. Both of mesoporous TiO₂ films revealed no trace amount of fluoride-related contaminant in XPS analysis (S2-2).¹⁻⁴

S1-2 DSSC preparation

A photoanode of DSSC was fabricated using TiO₂ paste of NS and NP on fluorine doped tin oxide (FTO) transparent conducting oxide glass (TCO22-7, Solaronix) by employing the doctor blade technique. Photocurrent-voltage characteristics of DSSC were measured with the device configuration composed of the mesoporous TiO₂ layer (~10 μ m) and opaque TiO₂ scattering layer (~5 μ m). Whereas, transparent cell configuration composed of thin TiO₂ films (~4 μ m) without scattering layer were applied for the analyses of electron transport dynamics by transient absorption spectroscopy and transient photocurrent-voltage including charge extraction method. Therefore on the first mesoporous TiO₂ layer coated on FTO substrates dried at 125°C on a hot plate, the second TiO₂ scattering layer was subsequently deposited by the same doctor blade technique with using commercially available paste (Ti-nanoxide D/SP, Solaronix). The TiO₂ films were then baked at 500 °C for 30 min. TiO₂ films were then dipped into a 0.5 mM Ru dye (N719, Solaronix) in *tert*-butanol (TBOH) and acetonitrile (AN) mixed solution (volume ratio of 1:1) for 16 h at room temperature. After the dye adsorption, these dye-sensitized TiO₂ films were then rinsed three times with ethanol to remove physi-sorbed dyes on the substrate, and then dried under nitrogen stream. A Pt-coated FTO glass as the counter electrode was prepared by spin-coating of H₂PtCl₆

aqueous solution (0.02M) on FTO and subsequently annealing at 400 °C for 30min in an oven. A 60 μm-thick sealant film (Meltonix 1170-60, Solaronix) was used as the spacer and sealant of dye-sensitized TiO₂ films and Pt counter electrodes. Finally the fabrication of the DSSCs was completed by injecting an electrolyte solution consisting of typically LiI (500 mM), iodine (50 mM), 4-*t*-butylpyridine (580 mM) and ethyl-methyl-imidazolium dicyanoimide (600 mM) in AN and valeronitrile (volume ratio of 85:15), while the varied contents of electrolyte were indicated in the main section. The cell area was typically 0.16 cm² and was precisely determined by measuring each sides of each device by a calliper.

S1-3 Device Characterization of DSSC

Photovoltaic properties of the fabricated DSSCs was measured by using a solar simulator (Yamashita Densho YSS-50A) equipped with a Xenon lamp for light exposure and a source-meter (Keithley, model 2400). The power of solar simulator were calibrated to 100 mW/cm² as AM 1.5 using a standardized silicon solar cells (PEC-SI01, Peccell Technologies, Inc.) before the measurement of each cells. The current-voltage characteristics were measured under the simulated solar irradiation to evaluate the photovoltaic parameters such as short-circuit current density (J_{SC}), open circuit voltage (V_{OC}), and the fill factor (FF) in order to estimate the conversion efficiency (η) as the relationship of;

$$\eta(\%) = J_{sc}(\text{mA}/\text{cm}^2) \times V_{oc}(\text{V}) \times FF \quad (\text{S1-1})$$

Spectral response as a function of the wavelength also known as the photocurrent action spectrum of the DSSCs, was measured with a constant photon flux at each wavelength in the DC mode. A photocurrent action spectrum measurement system (CEP-2000, Bunko Keiki) was used. Upon the illumination of the constant flux of monochromatic light, the generated photocurrent J_{SC} (mA/cm²) was used to calculate the incident photon-current conversion efficiency (IPCE). The monochromatic photon flux density was monitored by Si photodiode. IPCE was calculated by the following equation. $\text{IPCE} = N_e/N_p$ where N_e and N_p stand for exposure light dose and photocurrent respectively

S1-4 Electrochemical and Photo-electrochemical Characterization of TiO₂ films

Photo-electrochemical measurement of TiO₂ films with NS and NP TiO₂ were performed in a 0.1M LiClO₄ in acetonitrile supporting electrolyte solution in a three component electrochemical cell configured with platinum wire counter electrode and Ag/Ag⁺ reference electrode. The reference electrode was calibrated by independently measured redox potential of ferrocene (0.01M) with supporting electrolyte of 0.1M LiClO₄ in acetonitrile solution before and after the sample measurements. The cyclicvoltammetry of N719/TiO₂ was performed under scan rate of potential sweep of 50mV/sec. The optical absorption measurement under applied potential of TiO₂ films was also taken place with similar setup with 0.2M NaClO₄ aqueous supporting electrolyte solution and a reference electrode (Ag/AgCl), and which was introduced into the measurement cavity of UV-vis absorption spectrometer (V-570-DS, JASCO Inc.). The extra care was taken for the UV-vis absorption measurement under applied potential, so that none of electrochemical component, counter and reference electrodes did not interrupt the optical path for the optical measurements.

S1-5 Transient Photoelectrochemical Measurements

Similar solar cell device configurations were used to determine the electron transport dynamics based on the transient properties of device under the photoexcitation based on the stopped light incident measurement of photo current and voltage (SLIM-PCV) reported by Nakade *et al.*⁶ The sample was configured with the electronic system with response time of $<150\mu\text{sec}$ for monitoring the transient change of either J_{SC} or V_{OC} by a digital multimeter under a synchronized monochromatic light source as an expanded light of the solid state laser diode (642nm, Cube, Coherent Japan) controlled by an analog voltage signals supplied from a function generator (NF1974, NF) as reported elsewhere.⁶ The obtained transient curve was fitted to single exponential decay, therefore the time constant, τ_n and τ_c , of V_{oc} decay and inversed half lifetime of J_{SC} , respectively, under slight change (within $\sim 5\%$) of incident laser intensity. These time constants of τ_n and τ_c were calculated to the lifetime of electron carrier in TiO_2 mesoporous films recombining with mainly the oxidized iodide in the electrolyte solution, and transport diffusion coefficients, D_n , of electron in TiO_2 , respectively, as indicated with equation S1-2. The observed sets of τ_n and D_n under varied incident laser intensity were correlated with the carrier density in TiO_2 mesoporous films, which was independently determined by a series of charge extraction analysis as previously reported^{7,8}. DSSC cell was configured with a solid state switch opening and closing the circuit, which is controlled by a signal generator synchronizing the timing of switching with the signal control of incident light. In this setup, the extracted charges from the DSSC system, especially the electrons in TiO_2 mesoporous films, are counted under working condition of either open-circuit or short-circuit as the carrier density. Consequently the carrier lifetime, τ_n , and diffusion constant, D_n , in TiO_2 were plotted as a function of the carrier density in mesoporous TiO_2 films. TiO_2 thin films with the thickness of $4\mu\text{m}$ without scattering layer were applied to approximate the equal distribution of carrier generation through the TiO_2 films⁶. The charge density was determined based on the assumption of the uniform distribution of the charge throughout TiO_2 films by applying the equation (S1-3) with cell area, A , film thickness, t , and porosity, p , of mesoporous TiO_2 films.

$$D_n(\text{cm}^2\text{sec}^{-1}) = \frac{L^2(\text{cm}^2)}{2.77 \times \tau_c(\text{sec})} \quad (\text{S1-2})$$

$$N_n(\text{cm}^{-3}) = \frac{N_{obs}}{A(\text{cm}^2) \times t(\text{cm}) \times (1-p)} \quad (\text{S1-3})$$

S1-6 Femtosecond Transient Absorption Spectroscopy (TAS)

In the TAS setup, the laser source was a titanium/sapphire laser (CPA-2010, Clark-MXR Inc.) with a wavelength of 775 nm, a repetition rate of 1 kHz, and a pulse width of 150 fs. The light was separated into two parts. One part was used as a probe pulse. The other part was used to pump an optical parametric amplifier (OPA) (a TOAPS from Quantronix) to generate light pulses with a wavelength tunable from 290 nm to $3\mu\text{m}$. It was used as a pump light to excite the sample. In this study, a pump light wavelength of 532 nm and a probe beam wavelength of 775 nm were used with the circular exposed area with diameter of 3mm and 2mm, respectively. The pump light was modulated by using a chopper with a frequency of 140 Hz. The transient absorption change of the probe beam through the sample induced by the pump light

was detected by using a silicon diode detector (Model 2031, Newport) and a lock-in-amplifier. The pump and probe light intensity were 5 $\mu\text{J}/\text{pulse}$ and 2 $\mu\text{J}/\text{pulse}$, respectively⁹.

S1-7 TiCl_4 Treatment

To improve the DSSC properties, TiCl_4 treatment was carried out only with the sample to achieve the best efficiency as indicated in the main section. An aqueous solution of TiCl_4 (0.04M) was prepared with commercially available TiCl_4 in HCl_{aq} . Solution (0.09M in HCl_{aq} , Aldrich) by dilution with DI water. Then annealed TiO_2 films on FTO in a oven were immersed in the TiCl_4 solution at 70°C for 30min. After the treatment, the sample films were washed by DI water and ethanol followed by drying under N_2 stream. After TiCl_4 treatment, TiO_2 films were annealed in an electric oven at 500°C for 30 min, and then cooled samples were immersed in the dye-sensitizer solutions with exactly same procedure for device preparations as described above in S1-2.

S2. Characterizations of TiO₂ Nanoparticles and Mesoporous Films

S2-1 Characterizations of Mesoporous TiO₂ Films

Transmittance spectra of each mesoporous TiO₂ films (thickness of ~4 μ m) were obtained in the UV-vis region, 200-800nm, by a UV-vis spectrometer (V-570-DS, JASCO Inc.) with transmission mode. The transmittance of each films revealed almost identical in the UV-vis region. Therefore this indicates that the optical scattering characteristics of each films were identical. The powder x-ray diffraction (MiniFlex, Rigaku, Japan) was measured with the annealed TiO₂ mesoporous films revealing the expected diffraction peaks, which all are attributed to anatase TiO₂ with all of samples.

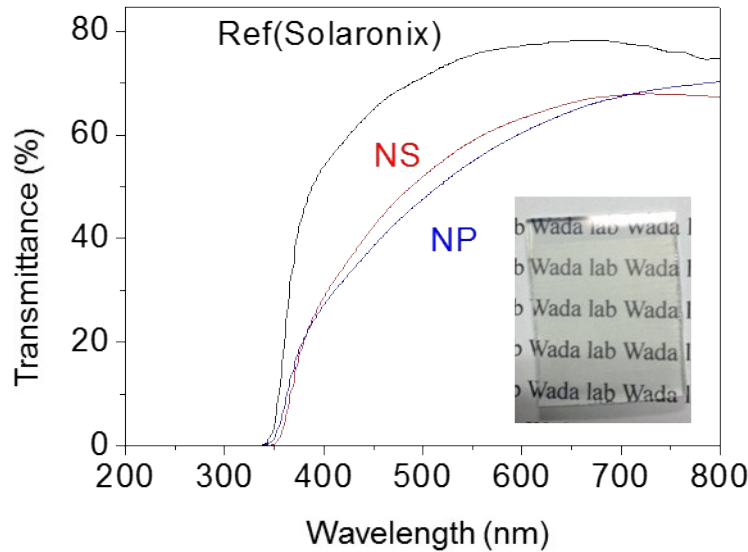
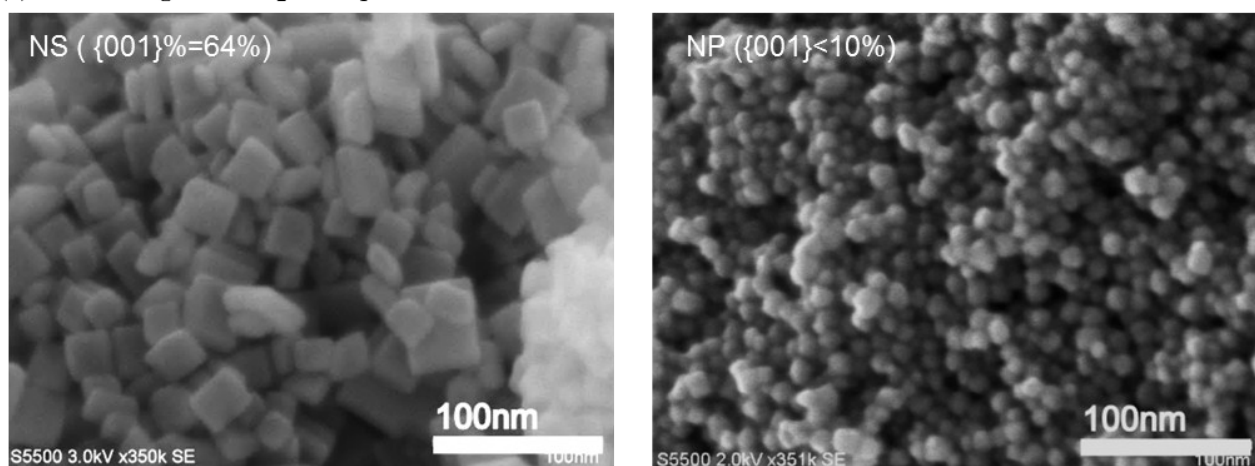
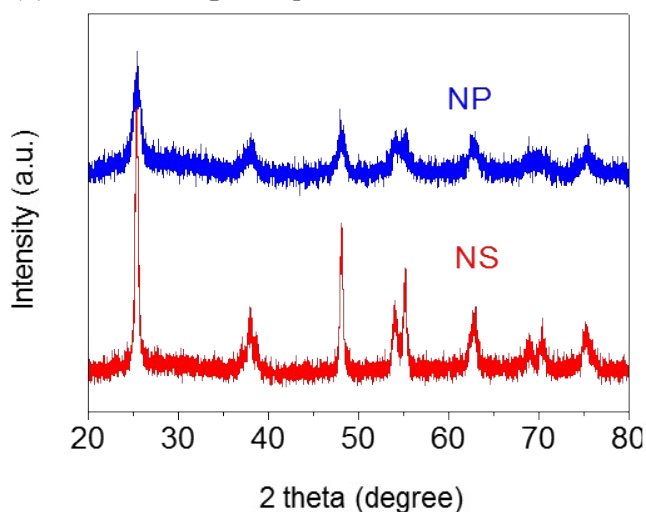


Figure S2-1 Transmittance spectra of TiO₂ films (~4 μ m thick) prepared either with {001}-dominant NS (red) or {101}-dominant NP (blue) TiO₂ nanoparticles coated on glass substrate indicating identical transmittance characteristics. The commercially available TiO₂ paste (~4 μ m thick, Ti-nanoxide T/SP, Solaronix) is also indicated as a reference.

(a) SEM image of TiO₂ nanoparticles



(b) XRD of TiO₂ nanoparticles



(c) XPS of TiO₂ nanoparticles

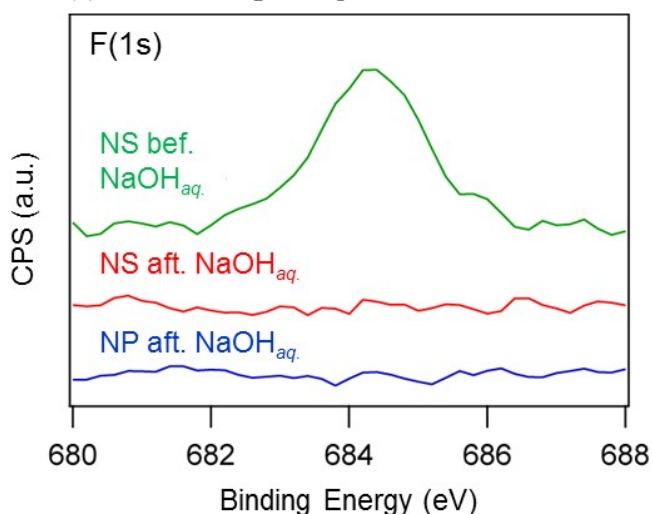


Figure S2-2 (a) SEM images and (b) XRD of each as-synthesized NS and NP TiO₂ nanoparticles. The fraction of {001} of NS was calculated by the averaged diameter in *a* and *c* axis of decahedral anatase TiO₂ crystals in SEM images. (c) XPS in fluorine (1s) region indicates that NS and NP has no residual fluorine contamination, which could be induced by the HF in the particle synthesis as observed with NS before NaOH_{aq.} decantation.

S2-2 Characterizations of Anatase TiO₂ Nanoparticles

Based on the ideal decahedral anatase TiO₂ crystal indicated in Figure S2-3, we determined the geometric values of synthesized TiO₂ nanoparticles from mean diameter in *a* and *c* axis measured in SEM images (Figure S2-2) as summarized in Figure S2-3. According to the assumption of inter-plane angle between (101) and (001) faces to be $\theta=68.3$ degree¹⁻³, we calculated values of *d* and *L* geometrically and summed surface areas of {001} and {101} facets, $S_{(001)}$ and $S_{(101)}$, respectively⁴. The fraction of {001} facets were determined from $S_{(001)}/(S_{(001)}+S_{(101)})$.

$$d = \frac{c/2}{\sin(68.3^\circ)} \quad (\text{S2-1})$$

$$L = a - \frac{2 \times (c/2) \times \cos(68.3^\circ)}{\sin(68.3^\circ)} \quad (\text{S2-2})$$

$$S_{(001)} = 2 \times L \times L \quad (\text{S2-3})$$

$$S_{(101)} = 8 \times (a + L) \times d / 2 \quad (\text{S2-4})$$

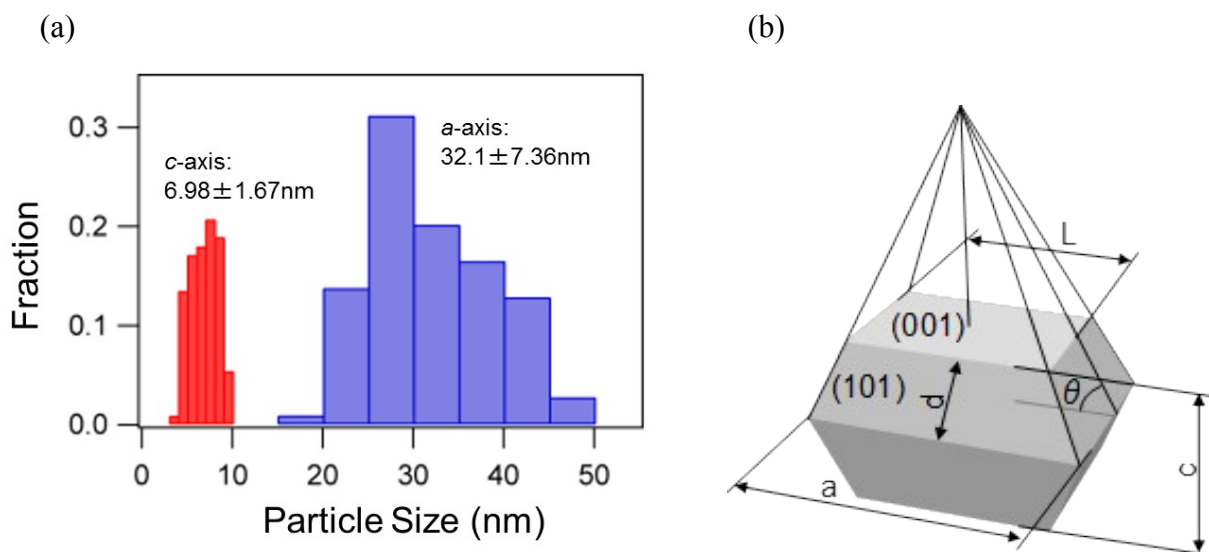


Figure S2-3 (a) The distribution of TiO₂ nanoparticle diameters in *a* and *c*-axis observed in SEM were exhibited for NS TiO₂ nanoparticles by analyzing more than one hundred of nanoparticles. The fraction of {001} of NS was calculated by the averaged diameter in *a* and *c*-axis of decahedral anatase TiO₂ crystals as the modeled ideal anatase TiO₂ nanoparticle structure (b).¹⁻³

S3 DSSC Properties

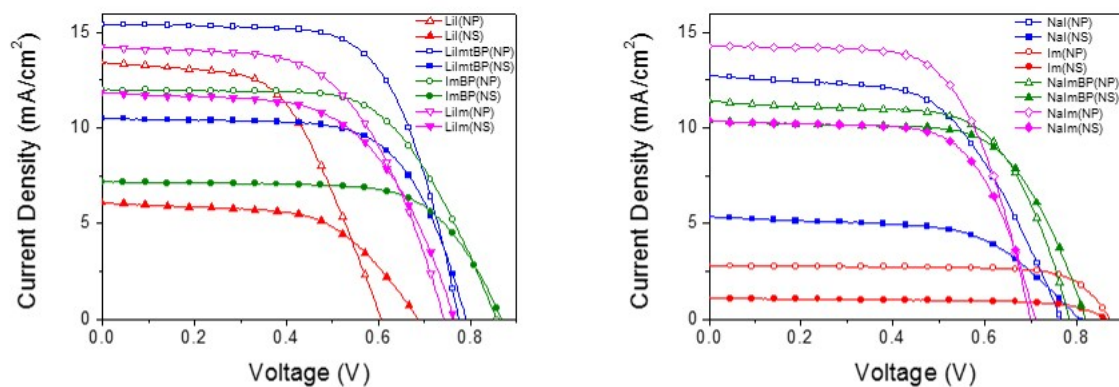


Fig S3-1 J - V characteristics of DSSCs with electrolyte of LiI, NaI, Im, ImBP, LiIm, LiImtBP, NaIm, and NaImtBP and TiO₂ film of NS (filled) and NP (opened) as the representative curves chosen from multiple samples. TiO₂ films ($\sim 10\mu\text{m}$) with scattering layer ($\sim 5\mu\text{m}$) are prepared to be identical for both NS and NP achieving complete light harvesting.

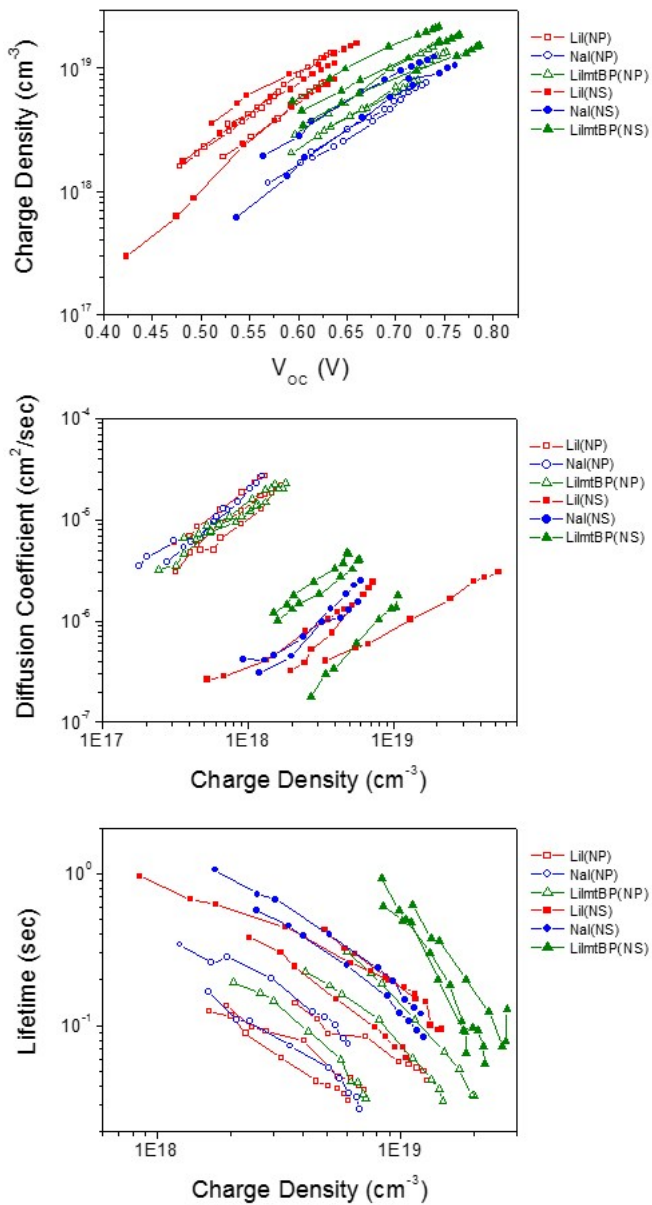


Fig S3-2 The device-to-device deviations of (a) charge density indicating the density of trap states below CB of TiO_2 as the function of open-circuit voltage determined by the charge extraction method, (b) electron diffusion coefficient, and (c) lifetime of electron in TiO_2 determined by SLIM-PCV of DSSCs with electrolyte of LiI (red), NaI (blue), and LiImtBP (green) and TiO_2 film of NS (filled) and NP (opened).

S4. Diffusion Length of Electron in TiO₂ Mesoporous Films in DSSC Configurations

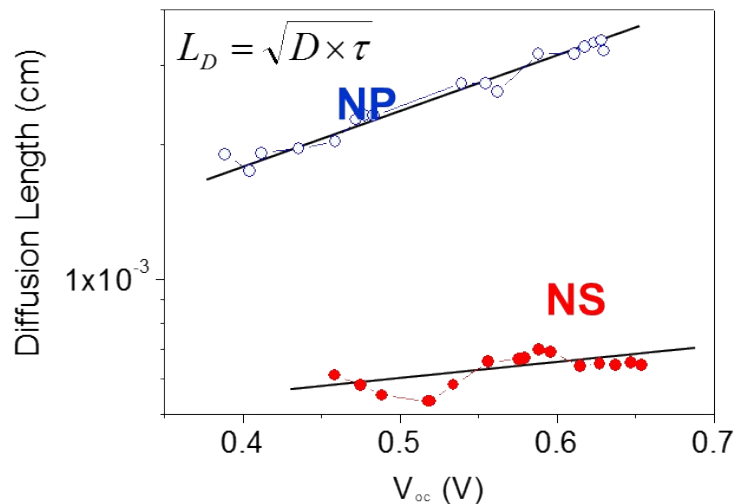
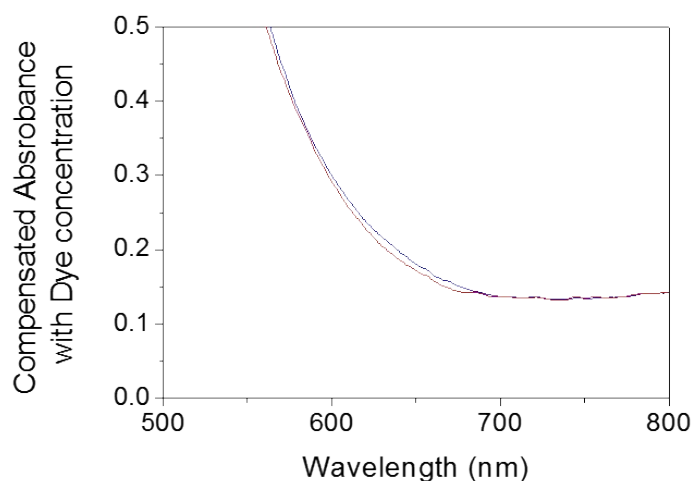


Figure S4-1 Diffusion length of each NS (red) and NP (blue) facet-dominant TiO₂ films calculated from diffusion coefficient and lifetime of electron in DSSC with LiI electrolyte. The curves of each diffusion coefficient and lifetime in Figure 3 was extrapolated with exponential fitting to provide the diffusion length, $L_D = \sqrt{D\tau}$, as the function of the open-circuit voltage.

S5. HOMO/LUMO Characterization of Dye-sensitizer on TiO₂ Mesoporous Films

(a)



(b)

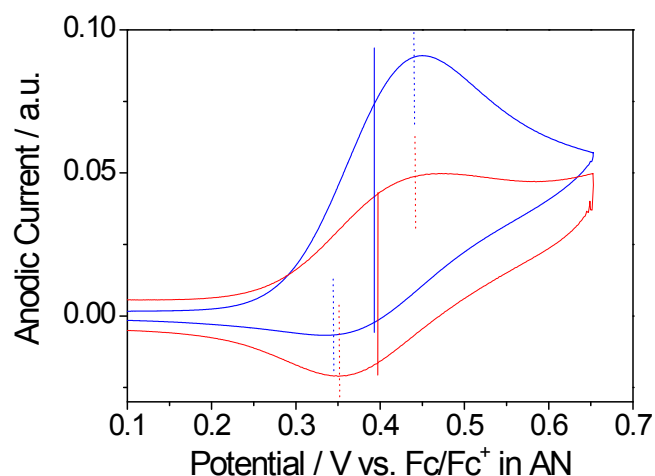


Figure S5 (a) Optical absorbance of N719/TiO₂ films with NS (red) and NP (blue) TiO₂ obtained by the transmission UV-vis absorption spectroscopy in closed DSSC device configuration with LiI electrolyte and glass plate instead of counter electrode. The absorbance data were normalized by the adsorbed amount of dye-sensitizer for compensating the difference of the adsorbed dye amount on NS and NP TiO₂. (b) Electrochemical cyclic voltammetry of N719/TiO₂ films with NS (red) and NP (blue) TiO₂ obtained in 0.1M LiClO₄ in acetonitrile solution in a three component electrochemical cell configured with platinum wire counter electrode and Ag/Ag⁺ reference electrode, which was pre-calibrated by independently measured redox potential of ferrocene (0.01M) with supporting electrolyte of 0.1M LiClO₄ in acetonitrile solution.

S6. TAS Results of Dye-sensitizer on TiO₂ Mesoporous Films in DSSC Configurations

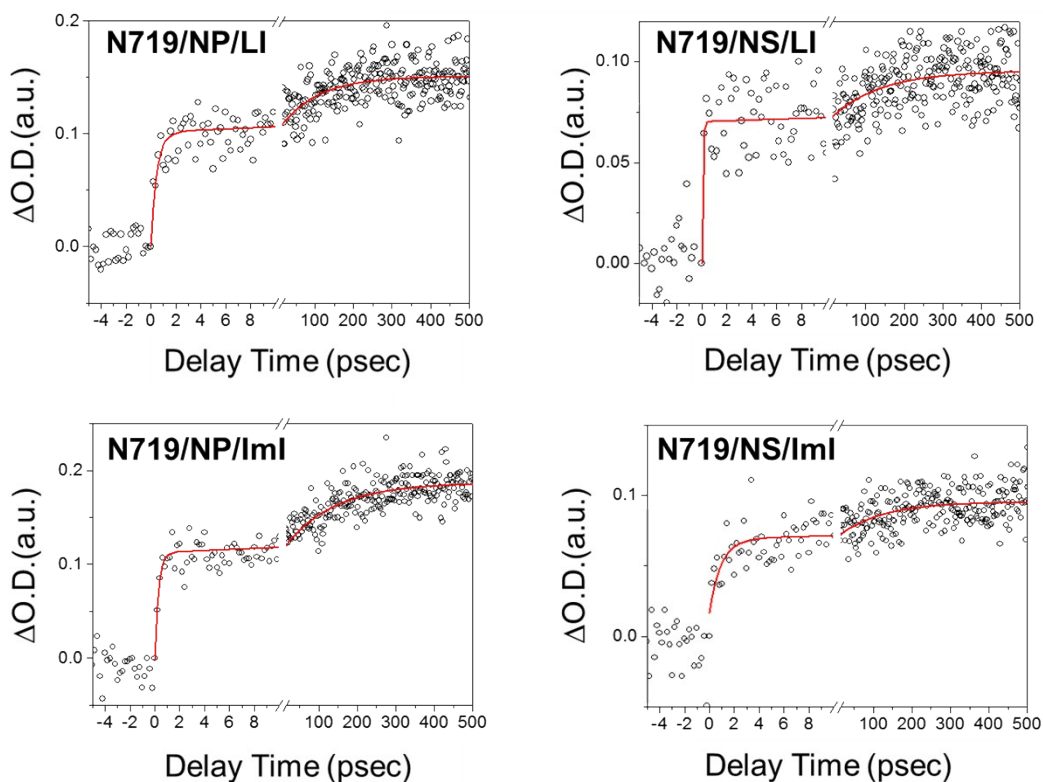
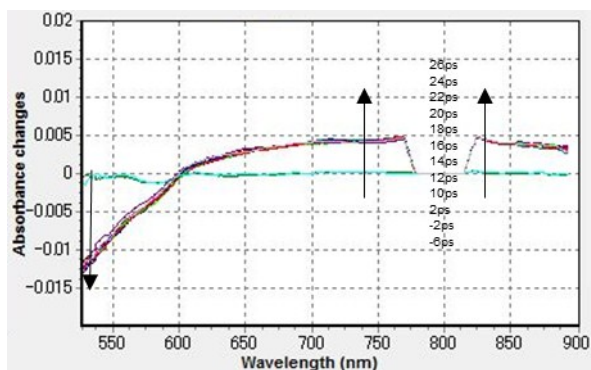
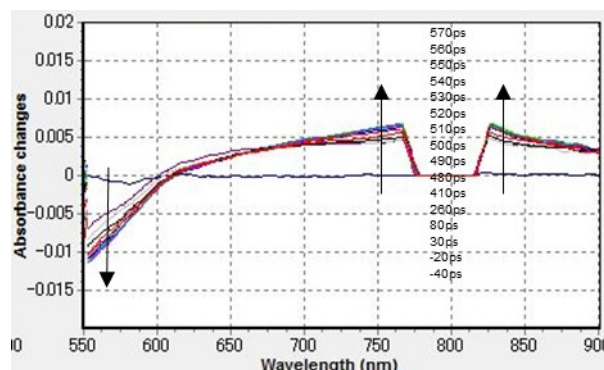


Figure S6-1 Transient absorption rise of oxidized N719 probed at 775nm on each NS and NP TiO₂ films (~4 μ m thick) in DSSC closed cell configuration under short-circuit condition.

(a) Visible region (short-term)



(b) Visible region (long-term)



(c) NIR region (long-term)

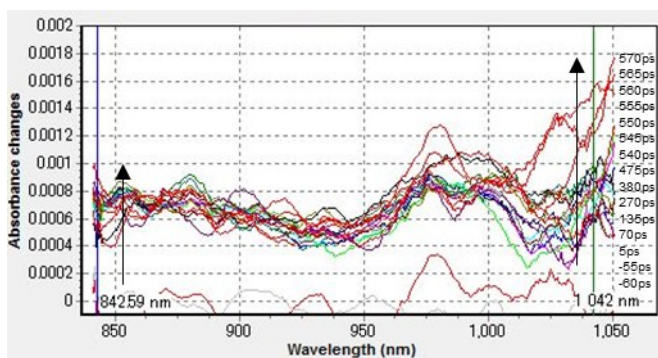


Figure S6-2 Subpicosecond transient absorption spectra of N719 on TiO_2 films ($\sim 4 \mu\text{m}$ thick) in DSSCs under short-circuit condition in the visible (a) and (b), and the NIR region (c). Transient absorption spectra were measured on hermetically-sealed DSSCs with a pump-probe method. Pump laser pulses (wavelength: 492 nm) were generated with an OPA system (Light Conversion TOPAS-C) excited by an 800 nm subpicosecond laser pulses from an amplified Ti: sapphire laser system (a pulse width of 130 fs, and a repetition rate of 1.0 kHz, Spectra Physics Hurricane). Probe white light continuum pulses were generated by focusing the 800 nm laser pulses on a 3 mm thick sapphire crystal plate. The transmitted probe beams were dispersed using a monochromator ($f = 250 \text{ mm}$) installed with a holographic grating (150 gr/mm, $\lambda_{\text{blaze}} = 700 \text{ nm}$), and were detected with a 1024-pixel InGaAs CCD detector. The absorbance change, $\Delta\alpha$, is calculated by $-\log[T_{\text{pump}}(\lambda)/T_{\text{w/o pump}}(\lambda)]$, where $T_{\text{pump}}(\lambda)$ and $T_{\text{w/o pump}}(\lambda)$ are the transmitted probe beam signals obtained with pump beams and without pump beams, respectively. An instrument response function of the system is about 250 fs. The spectra (a)-(c) exhibit the time evolution of oxidized state of N719 after pulsed excitation. The absorption increase in the visible region (from 600 nm to 800 nm) is attributed to the absorption of oxidized ruthenium dye cation created by the photoinduced electron injection to TiO_2 . The absorption increase in the NIR region ($\sim 1000 \text{ nm}$) is assigned to the carrier absorption in TiO_2 caused by photoinduced electron transfer from the dye. The dip appearing around 800 nm is artifact due to a signal saturation of the detector.

S7 TiCl₄ Treatment for Improving DSSC Properties

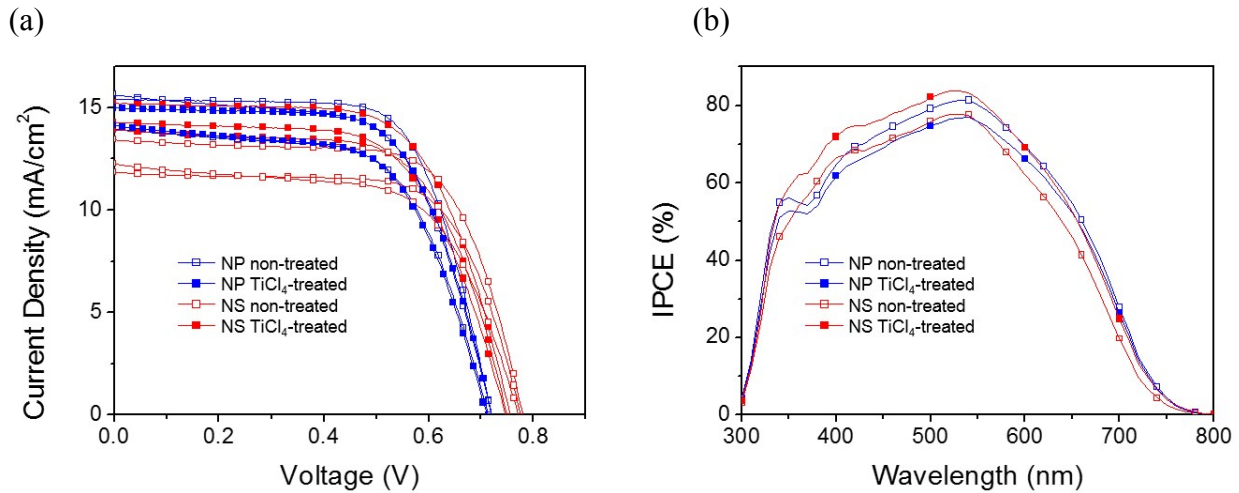


Fig S7-1. (a) J - V and (b) IPCE characteristics of DSSCs with electrolyte of LiImtBP and TiO₂ film of NS (red) and NP (blue) with (fill) and without (open) TiCl₄ treatment. Thickness of TiO₂ films (~10 μm) with scattering layer (~5 μm) are prepared to be identical for both NS and NP achieving complete light harvesting efficiency of DSSC with revealing the device-to-device deviations.

Table S7-1. Photovoltaic properties of DSSC by using NS and NP with and without TiCl₄ treatment.

	NP		NS	
	Non-treated	TiCl ₄ treated	Non-treated	TiCl ₄ treated
J_{SC} (mA/cm ²)	15.02 ± 0.92	15.07 ± 0.95	12.54 ± 0.83	14.48 ± 0.68
V_{OC} (mV)	720.2 ± 5.5	718.6 ± 4.8	777.5 ± 2.8	752.5 ± 4.8
FF (%)	64.5 ± 3.2	63.6 ± 1.9	66.4 ± 3.6	64.3 ± 1.2
Conversion Efficiency (%)	6.98 ± 0.68	6.89 ± 0.60	6.48 ± 0.63	7.01 ± 0.43

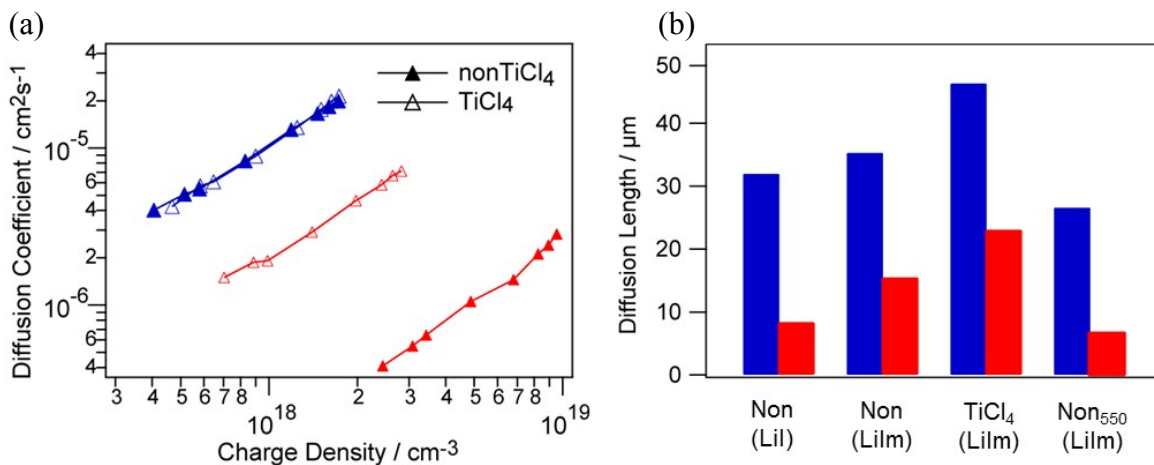


Fig S7-2. (a) Diffusion coefficients with electrolyte of LiIm and (b) diffusion length of electron with electrolyte of LiI and LiIm in DSSCs with TiO₂ films of NS (red) and NP (blue) with (open) and without (filled) TiCl₄ treatment with the films thickness of 4 μm. Non550 indicates TiO₂ annealed at 550°C.

REFERENCES

- (1) Yang, H. G.; Sun, H. S.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. *Nature* **2008**, *453*, 638-641.
- (2) Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L. *J. Am. Chem. Soc.* **2009**, *131*, 3152-3153.
- (3) Wang, X.; Liu, G.; Wang, L.; Pan, J.; Lu, G. Q.; Chen, H. M. *J. Mater. Chem.* **2011**, *21*, 869-873.
- (4) Maitani, M. M.; Tanaka, K.; Mochizuki, D.; Wada, Y. *J. Phys. Chem. Lett.* **2011**, *2*, 2655–2659.
- (5) Ito S., *Dye-sensitized Solar Cells*, (Eds: K. Kalyanasundaram), EPFL Press, Lausanne, 2010, Ch. 8.
- (6) Nakade, S.; Kanzaki, T.; Wada, Y.; Yanagida, S., *Langmuir*, **2005**, *21*, 10803-10807.
- (7) Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U., *Electrochem. Commun.*, **2000**, *2*, 658-662.
- (8) O'Regan, B. C.; Bakker, K.; Kroeze, J.; Smit, H.; Sommeling, P.; Durrant, J. R., *J. Phys. Chem. B* **2006**, *110*, 17155-17160.
- (9) Shen, Q.; Katayama, K.; Sawada, T.; Hachiya, S.; Toyoda S. *Chem. Phys. Lett.* **2012**, *542*, 89–93.