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Effects of energetics with {001} facet-dominant anatase TiO₂ scaffold on electron transport in CH₃NH₃PbI₃ perovskite solar cells

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Abstract

The anatase titania with large fraction of {001} facet on the mesoscopic anatase titania scaffold in the hybrid perovskite solar cells exhibited higher photocurrent and open-circuit voltage. The higher performance with {001}-dominant anatase titania with the fraction of 74% were discussed with the characteristic electron transport properties in addition to the energy levels of trap states and conduction band as compared with those properties of conventional anatase titania scaffold. The resulted higher photocurrent and open-circuit voltage were attributed to the enhancement of the electron injection and suppression of the carrier recombination, respectively, at the titania/perovskite semiconductor interface.

Keywords:

TiO₂

Mesoporous

Facet

Electron transport

Perovskite solar cell

1. Introduction

The hybrid organic-inorganic metal halide hybrid semiconductors possessing perovskite crystalline structure have been utilized for one of the most promising printable solar cells, perovskite solar cells (PSCs), due to its ease of fabrication with potentially low-cost materials, and remarkably high conversion efficiency of more than 22% [1e6]. Owing to the large efforts of process engineering, the device fabrication processes have been well-optimized to achieve the conversion efficiency close to the maximum limit of optical absorption with methylammonium lead iodide (CH₃NH₃PbI₃) hybrid perovskite semiconductor [7]. To further improve the conversion efficiency, the absorption range has to be

extended to the longer wavelength region, such as near-infrared (NIR), to match the action spectrum of device with the solar spectrum [8e21]. The ABX₃ perovskite construction is potentially engineered by applying novel cations, A [10e14], metals, B [15e18], and anions, X [19e22], to manipulate the bandgap determining the photo absorption. However, extending light harvesting property to longer wavelength, i.e. possessing lower photon energy, results in the band gap narrowing of hybrid perovskite semiconductor and typically lowers the overall efficiency, although the photocurrent is improved [17,18]. This is typically due to less efficient electron and hole transfer to either electron transport layer (ETL) or hole transport layer (HTL) with narrow bandgap perovskite than those carrier transfer processes in the state-of-art CH₃NH₃PbI₃ based

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PSCs achieving more than 20% of conversion efficiency by owing to appropriate energy matching. Nevertheless, this issue potentially becomes significant once the narrow bandgap perovskite semiconductor is utilized for extending the photon harvesting property [22e25]. Under these circumstances, elucidating interface chemistry becomes important to achieve the efficient electron transfer.

As anatase titania (TiO_2) has been majorly utilized for the ETL, we focus on the facet effects of the anatase TiO_2 on PSC. The exposed facet control of anatase TiO_2 nanoparticle has been recently achieved by utilizing surfactant chemistry to engineer the surface energy of nanoparticles [26e29]. The surfactant additives selectively enlarge relatively unstable {001} or {100} facets possessing high surface energy to the most stable {101} facet on anatase TiO_2 nanoparticles; e.g. {101} facet is supposed to cover more than 95% of whole surface of anatase TiO_2 under natural synthetic environments [30,31]. Following the reports, many works have studied facet effects of TiO_2 nanoparticles on photo electrochemical reactivity [27,29], adsorption desorption nature [32,33], carrier transport properties [34e36], and applications to photocatalysts [37,38], battery materials [39], and opto-electric devices including solar cells [40e46].

In the application of the facet-dominant TiO_2 nanoparticles to PSCs, a few of experimental studies have been performed with the {001} facet-dominant anatase TiO_2 nanoparticles for the applications to the scaffold of PSC, while the detailed study is still limited [42,43]. Recently, a report proposed the favorable matching of the lattice constant in hybrid perovskite semiconductors onto certain facet orientations of TiO_2 scaffolds [47]. In addition, a few reports have also suggested that the issues of PSC related to efficiency and stability involved with current-voltage hysteresis could be attributed to the imperfection of the interface, such as the chemical interactions [48e50], band alignment [51e53], and lattice mismatch [47,54]. Therefore the adequate selection of the crystalline orientation of the scaffold could be one of key elements to construct proper interfaces of PSC for improving overall device performances.

Since the anatase TiO_2 as the scaffold of PSC attains the highest efficiency [1e6,10,22], detailed studies of the surface chemical effects of anatase TiO_2 scaffold on PSC properties bring the most significant impact on the construction of ideal interface for high performance of cells. Furthermore, previous report suggested either {001} facet of rutile or anatase phase had a low lattice mismatch of less than ~5% with $\text{CH}_3\text{NH}_3\text{PbI}_3$, while conventionally applied {101} facet of TiO_2 possesses the larger lattice mismatch [47,54]. We, consequently, focus on dominantly exposed facet of anatase TiO_2 nanoparticles and systematically varied the fraction of the {001} facet of anatase TiO_2 nanoparticles to construct the mesoporous scaffold in PSC. The device characteristics are examined with identical device configuration prepared with 2-step deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid perovskite semiconductor films. The devices with TiO_2 scaffold exposing largest fraction of {001} facet exhibits the highest efficiency, and are correlated with the electron transport properties evaluated by the electrochemical impedance spectroscopy (EIS). In addition, the TiO_2 band-gap state so-called electron trap states are analyzed by the reversed double-beam photoacoustic spectroscopy (RDB-PAS) to examine the energy-resolved distribution of electron traps (ERDT) [55e57]. The effects of {001} facet dominant anatase TiO_2 as the scaffold are discussed based on the energetics of TiO_2 scaffold and resulted electron transport in cells to potentially boost the conversion efficiency of PSCs.

2. Experimental

2.1. Hydrothermal synthesis of anatase TiO_2

The conventional hydrothermal synthesis previously reported

was applied to synthesize a series of {001} facet-dominant anatase TiO_2 nanoparticles as details of synthesis are summarized elsewhere (S1) [35,58]. The synthetic procedure typically consists of a precursor solution composed of tetrabutoxytitanium (IV) ($\text{Ti}(\text{OBu})_4$, 25 mL) and aqueous hydrofluoric acid solution (HF, 3 mL) with varying concentrations to change the resulted fraction of {001} facet (S2). The mixed precursor solution was tightened in a Teflon-lined autoclave container and kept at 180 °C for 24 h in an oven. 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 (0.1 M) and then rinsing with distilled water until pH 7.0 was achieved in order to remove fluorinated titanium products on TiO_2 surface [26,35,58]. The washed samples were confirmed that there is no fluorinated compound as the contamination of the surface by XPS analysis [35].

2.2. Preparation of anatase TiO_2 paste

Earned TiO_2 nanoparticle suspensions in ethanol were then processed to prepare a TiO_2 paste for creating mesoporous TiO_2 films by adding binders of α -terpineol and of ethylcellulose dispersed in ethanol [59]. The mixed suspensions composed of TiO_2 (2.73 wt%), ethanol (84.8 wt%), α -terpineol (11.1 wt%), and two kind of ethylcellulose (18e22 mPa with 0.77 wt%, and 45e55 mPa with 0.60 wt%) were homogenized under ultrasound sonic hone with titanium rod followed by ball milling with zirconia beads for 20 h. Finally the ethanolic solvent was evaporated by rotary evaporator under 45 °C to earn the 8e10 wt% of TiO_2 as the stock suspension paste. Each TiO_2 mesoporous film was prepared by diluting those TiO_2 pastes with a corresponding amount of ethanol and spin-coated on substrates in order to control the identical TiO_2 film thickness and optical scattering properties (S2).

2.3. Perovskite solar cell device construction

The perovskite solar cells (PSCs) were fabricated by constructing layers of compact TiO_2 , mesoporous TiO_2 , $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, organic hole transport layer (HTL), and metal counter electrode on a fluorine doped tin-oxide as the transparent conducting oxide glass (FTO, TEC-15, Nippon Sheet Glass Co. Ltd.) by mainly employing the wet coating processes [60]. Firstly, the compact TiO_2 layer was deposited by an aerosol spray pyrolysis of titanium diisopropoxide bis(acetylacetonate) solution in isopropanol (75%, Sigma-Aldrich) diluted with 9-equivalent volume of ethanol onto FTO substrates located on a hotplate heated at 500 °C under ambient atmosphere. After cooled to room temperature (~25 °C), the substrates were kept in an aqueous solution (0.04 M) of titanium tetrachloride (0.09 M diluted in HCl, Sigma-Aldrich) for 30 min at 70 °C, then washed by distilled water, dried under nitrogen gas, and finally annealed in an oven at 500 °C for 30min. And then each TiO_2 paste was spin-coated onto the compact TiO_2 . The spin-coating procedure were separately optimized with the top spinning rotation of around 3000e6000 rpm in order to achieve almost identical thickness of mesoporous TiO_2 layers possessing 280 nm $\pm$ 30 nm thick. The coated mesoporous TiO_2 was sintered in an oven for 30 min at 500 °C. After UV-ozone treatment was performed on TiO_2 surface for 15 min, then the PbI_2 (1.2 M, Aldrich) in N, N'-dimethylformamid (DMF) solution was spin-coated at the top spinning rotation of 6000 rpm for 10 s and dried at 70 °C on a hot plate for 30 min under dried nitrogen atmosphere. After drying the films, those samples were transferred into dry air chamber. Then, the PbI_2 films were immersed into an isopropanolic solution of methylammoniumiodide (50 mM) and kept for 20min in order to convert the films to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. The samples were then quickly

rinsed with isopropanol and annealed at 70 °C on a hot plate for 30 min under dried air atmosphere after spin-dried. After cooling the sample to room temperature (~25 °C), a solution to prepare spiro-MeOTAD HTL was spin-coated onto the perovskite films at the top spinning rotation of 4000 rpm for 30 s under dried air ambient; the spiro-MeOTAD solution was composed of 100 mg of spiro-MeOTAD, 40 mL of tert-butylpyridine (Sigma-Aldrich), 24.2 μ L of lithium bis(trifluoro methanesulfonyl)imide (520 mg/mL in acetonitrile stock solution), and 40 μ L of an organo-cobalt complex as dopant (300 mg/mL in acetonitrile solution, FK102, Dyesol) in 1 mL of chlorobenzene. And finally the PSC devices were completed by the vapour deposition of Au counter electrode (80 nm thick) in a vacuum thermal evaporator ($<10^{-6}$ torr).

2.4. Characterizations of materials and solar cell devices

Earned TiO₂ nanoparticles and films were examined by scanning electron microscopy (SEM, S-5500, Hitachi), x-ray diffractometry (XRD, MiniFlex, Rigaku), UV-vis spectroscopy (V-570-DS, JASCO Inc.). Photovoltaic performances of PSCs were evaluated as current-voltage characteristics under an AM 1.5 solar simulator (model 81172, Oriel) and the spectroscopic external quantum yield under monochromatic light (VE300, Bentham).

The EIS of each PSC device with different TiO₂ scaffold were measured at various DC bias voltages along the working regime of the cells (from short circuit to open circuit conditions) under AM1.5 irradiation. The modulated AC voltage perturbations had amplitude of 20 mV and a frequency of 0.4 MHz to 10 MHz range. Although the analyses of EIS taken with PSC are still under debates, we applied a simple model previously reported to extract the resistance and capacitance components of each RC elements based on a general equivalent circuit form the Nyquist diagram [60,62].

2.5. Electron trap density and bandgap measurement of TiO₂

The bare TiO₂ scaffold were examined in terms of electron trap density and band gap by means of reversed double-beam (RDB-) and single-beam (SB-) photoacoustic spectroscopy (PAS), respectively, with home-built PAS measurement setup utilizing modulated probe beam (80 Hz) irradiated to a sample cell where TiO₂ sample and microphone were placed for detecting the acoustic signal caused by optical absorption of samples [55,56]. The TiO₂ samples were prepared as TiO₂ films by doctor-blead method onto

glass substrates. Annealed TiO₂ films were shaved off the glass substrate to earn the powder sample to be placed in the sample cavity. RDB-PAS exhibits the optical absorption of trapped electron in the electron trap states of mesoporous TiO₂ scaffolds. The measurement was performed with purging an argon saturated with methanol vapour as the hole scavenger in the sample cell. SB-PAS exhibits the optical absorption as bandgap excitation of TiO₂ to determine the bandgap energy.

3. Results and discussion

The systematic difference of HF concentration in the precursor solution of TiO₂ nanoparticles exhibited the systematic variation of the surface fractions of {001} facet as determined by SEM images (S2). Therefore the estimated fractions of {001} facet revealed the facet fractions up to ~74% as shown in the SEM images of mesoporous TiO₂ scaffold films (Fig. 1a). All the obtained TiO₂ nanoparticles were found to be in the anatase phase from the XRD (S2). As SEM image indicates in Fig. 1a, series of NS TiO₂ exposing {001} facet can be spontaneously aligned with the anatase [001] perpendicularly to the substrate plane due to the sheet structure of nanoparticles. This orientation is also confirmed by the XRD of TiO₂ films (S2) in which series of NS TiO₂ exhibited relatively intense (004) peak at two theta of ~38° (S2), as we previously reported [62,63]. Since the perovskite film is constructed on the TiO₂ scaffold, the difference in morphology of TiO₂ could also affect to the interfacial properties. This difference of contact may be also involved in the observed properties in the devices assembled with NS TiO₂ as compared with NP. As NS TiO₂ provide the spontaneous alignment of {001} facets, this could be also one of the advantage to create the well-defined interface between TiO₂ and perovskite, while conventional spherical TiO₂ with random orientation could construct less oriented interface between TiO₂ and perovskite.

PSC devices were thus prepared on these TiO₂ scaffold films by using conventional sequential deposition of CH₃NH₃PbI₃ [60]. The main focus of our study here is a systematic comparison of device properties with variation of exposed anatase TiO₂ {001} facet fractions of mesoporous scaffold. For this purpose, all the cells were fabricated with identical device processes, which were confirmed with the identical featured in cross-section SEM images of PSC devices (Fig. 1b), in addition to the surface morphology, optical absorption, crystalline orientations and properties of perovskite films, as well (S3).

Fig. 1. (a) SEM surface images of anatase TiO₂ mesoporous scaffold on FTO substrates and (b) SEM cross-section images of PSC devices.

Fig. 2. (a) J-V characteristics under solar simulator (AM1.5) and dark, and (b) IPCE under monochromatic light of PSC devices incorporating each mesoporous TiO₂ scaffold layer.

Table 1
J-V characteristics under solar simulator (AM1.5) of PSC devices utilizing each mesoporous TiO₂ scaffold layer.

TiO ₂ scaffold	J _{SC} /mA cm ⁻²	V _{OC} /V	FF	Efficiency/%
NP	20.28 ± 0.25	1.059 ± 0.010	0.715 ± 0.015	15.36 ± 0.56
38% {001}	20.46 ± 0.39	1.033 ± 0.032	0.693 ± 0.036	14.69 ± 1.32
57% {001}	20.57 ± 0.32	1.042 ± 0.022	0.699 ± 0.033	15.02 ± 1.08
74% {001}	20.84 ± 0.18	1.057 ± 0.009	0.722 ± 0.010	15.91 ± 0.44

PSC performances were then evaluated based on the current-voltage (J-V) characteristics under a solar simulator (AM1.5) and incident photon-to-current conversion efficiency (IPCE) under monochromatic light (Fig. 2, Table 1, and S4). Observed J-V characteristics with each mesoporous TiO₂ scaffold are exhibited in Fig. 2 and each component of cell properties are summarized in Table 1 and Fig. 3. Although the hysteresis of forward and reverse scans in J-V property is one of the important issues in PSC, differences of hysteresis are not focused here, since the origin of hysteresis is still under the debate. In our discussion, the results of the reverse scan (scan from open-circuit to short-circuit) were mainly discussed to avoid the complexity of hysteresis, as most of literature have done so, while the whole results including hysteresis of each cell were also exhibited in S4. The short-circuit current, J_{SC}, shows improvement by incorporating {001} facet-dominant TiO₂ mesoporous scaffold (NS38%, NS57%, and NS74%) as compared with NP presumably with a smaller fraction of {001} (<~5%), since NP was synthesized without addition of HF [26,30,32,35]. Furthermore, J_{SC} systematically increased, as the fraction of {001} increased (Fig. 3). Since the IPCE of each cell with different TiO₂ scaffold revealed almost identical spectra with only height difference (Fig. 2), each scaffold at least exhibited identical optical properties without any characteristic scattering; i.e. transmittance spectra of bare TiO₂ scaffold films and perovskite films on each TiO₂ scaffolds also support this (S2 and S3). Therefore we assume that the origin of J_{SC} increase could be attributed to the differences in charge transport process as discussed in later section with EIS results. Another characteristic difference among different fractions of {001} in mesoporous TiO₂ scaffold is the open circuit voltage of each devices as observed in J-V characteristics (Figs. 2 and 3). As the fraction of {001} increased, the open-circuit voltage, V_{OC}, systematically increased except with NP, which was found to be out of trend. We further discuss the trend of voltage by considering the trap density in the later section.

As previous reports suggested correlations between {001} facet-dominant TiO₂ and differences in photoelectrochemical properties,

such as light scattering, charge transport, and interfacial electron transfer properties in photocatalysis and DSC systems [26e46], our results could be attributed to these factors. Since the scaffold may result in the different cell configurations, film morphology, perovskite crystallinity, and optical properties of cell, the SEM top views of the perovskite semiconductor films, cross-section of device configuration (Fig. 1), x-ray diffraction (XRD), and transmittance spectra of perovskite semiconductor films on each TiO₂ scaffold/FTO were examined (S3). According to these results, we at least conclude that there is not any significant difference with the fundamental properties of perovskite semiconductor films. Therefore, the difference in photocurrent and voltage of solar cells can be originated to other characteristics than the intrinsic differences of the prepared perovskite semiconductor films on each TiO₂ scaffold possessing different fractions of anatase {001} facet.

As discussed above, the differences of resulted solar cell performance can be attributed to the charge transport properties in the TiO₂ scaffold and at the perovskite/TiO₂ scaffold interface. We therefore analyzed the EIS response of each PSC device to investigate the differences in the interfacial charge transfer and capacitance properties of cells. The impedance spectra of each PSC device under illumination resulted in typical Nyquist plots (S4). Although the analyses of EIS taken with PSC are still under debate, we applied a simple model previously reported to extract the resistance and capacitance components of each RC elements based on a general equivalent circuit [60e62]. The extracted values of each resistance and capacitance components are exhibited as the function of the applied voltages for each PSC devices with different TiO₂ scaffold (Fig. 4).

The resistance component, R₁, shows significant divergences between NP and series of NS as well as certain dependence on the fraction of {001} facet. This component can be related to the transport resistance of the mesoporous scaffold including the interface between compact layer and mesoporous scaffold. In our previous study, the diffusion coefficient of the {001} facet-dominant anatase TiO₂ appeared lower as compared with conventional spherical anatase nanoparticles [46] probably because of a few hypothetical reasons, such as the intrinsic directionality of electron diffusion constant in terms of the crystalline orientation [64e66], imperfection of the inter-particle necking [66e68], higher density of boundaries in the direction of electron transport [66,68], and deeper distribution of trap state [69e72]. Therefore, the trend in the results of R₁ components revealed the sufficient consistency with the results we observed in DSC with utilizing the varied fraction of {001} facet-dominant anatase TiO₂ nanoparticles.

The component of R₂ is typically attributed to the recombination

Fig. 3. Plots of cell properties of (a) J_{sc} , (b) V_{oc} , (c) fill factor, FF, and (d) maximum conversion efficiency summarized from J-V characteristics of PSC devices utilizing each mesoporous TiO_2 scaffold layer.

resistance as similarly reported [73e75]. Since the recombination resistance is one of the determinant factor of the open-circuit voltage, the order of the resistance in the high voltage region around open-circuit voltage ($V_{app} \sim 0.9$ V) revealed the consistency with the order of the open-circuit voltage in J-V characteristics; i.e. higher R_2 appeared to be a correlation with higher open-circuit voltage in J-V characteristics (Fig. 3). Although the difference is small, this could indicate that the {001} facet-dominant anatase TiO_2 presents slower recombination rates. This seems to indicate that the achievable V_{oc} is mainly determined by the recombination, in agreement with previously published results in DSCs and PSCs [35,76e78]. However, it has not been yet clearly understood why {001} facet-dominant anatase TiO_2 slows down the recombination kinetics, although a few reports proposed the mechanism of the slower recombination with {001} facet-dominant anatase TiO_2 in DSC; e.g. geometrical factor related to the molecular orientation of adsorbates [33,44], larger potential gap between trap state and conduction band (CB) [46,70], recombination kinetics caused by slow diffusion [35,46,70,75], and density of state on the TiO_2 surface [72,75]. In any case, the peculiar characteristics of {001} facet dominant TiO_2 we observed here is that PSC devices also revealed consistent results to those in DSC in terms of slow recombination, and therefore the electron transport characteristics. These facts not just in the case of DSCs, but also in the PSCs clearly indicates that the origin is not from the proposed dye-orientation [46], but could be related to the interface chemistry between perovskite

semiconductor and TiO_2 , and thus could be related to more intrinsic properties of the {001} facet-dominant anatase TiO_2 in solar cell devices.

In terms of capacitance, C_1 probably related to the geometrical capacitance of the perovskite semiconductor, presents minor differences in the analyzed samples. On the other hand, relatively large capacitance was observed in the C_2 values. This capacitance, dominating the impedance response (particularly at lower frequencies) is generally related to the charge accumulation capability of the perovskite, as well as to giant dielectric features which are currently under scientific discussion.

To elucidate the origin of the enhancement of charge injection induced by {001} facet dominant TiO_2 , the analyses of band gap energy and ERDT were performed with bare mesoporous anatase TiO_2 scaffold by RDB-PAS under methanol saturated argon ambient in the sample cell, and SB-PAS under dry nitrogen ambient, respectively [55,56]. According to the results of SB-PAS (Fig. 5a), CB edge of TiO_2 determined by the absorption edge revealed that the CB shifts lower in energy level as the fraction of {001} increased. This trend of CB shift is consistent with a few of reported results [45], while the SB-PAS data revealed more precise results, since the data is mostly inert to the light scattering and other optical factors which would disturb determining the absorption edge with powder samples. Therefore, observed lower energy level shift of capacitance of C_2 with increase of the fraction of {001} facet observed in EIS (Fig. 4) could be directly correlated to the

Fig. 4. Parameters extracted from the fitting of the electrochemical impedance spectra of PSC devices utilizing each mesoporous TiO₂ scaffold layer. (Need colour change and sample name of 74% (red), NS 57% (yellow), NS38% (blue), and NP (green)). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. (a) CB edge determined by absorption spectra obtained by SB-PAS and (b) Trap density determined by RDB-PAS normalized at peak top with inset indicating the trap density in a specific surface area of each TiO₂ mesoporous scaffold exposing {001} facet with fractions of 74 (red), 57 (orange), 38 (blue), and ~5% (green) with line fit to determine the absorption edge. The molar absorptivity of trapped electrons was calibrated by referring the previous study [55e57]. The energy level was determined based on wavelength of absorption, therefore the calculated values based on the wavelength are ascribed as the energy level from valence band maximum (VBM) of each TiO₂ film. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

BrAsp on anatase $\text{TiO}_2(\{001\})$ for dye-sensitized solar cell applications, Phys. anatase TiO_2 indicated with absorption edge in SB-PAS as consistent with previous report [45]. In addition, the rise of trap density observed by RDB-PAS in Fig. 4b coincidentally revealed the similar trend of energy level shift of the bottom edge of trap state distribution in case the $\{001\}$ facet was increased from the fraction of 38% to 74%. On the other hand, NP supposedly possessing minimum fraction of $\{001\}$ facet exhibited out of this trend; i.e. the trap energy level and density displayed next to NS74%. This may be because the electron traps are mostly originated to the surface defects on TiO_2 have different nature on conventional facet of $\{101\}$ and novel facet of $\{001\}$ as discussed in previous studies [30,31]. The detailed discussion with electron traps are delivered in the next section. Consequently, the higher J_{sc} observed with introducing $\{001\}$ facet dominant TiO_2 could be due to more efficient electron injection process from perovskite by increasing the potential gap between CB of perovskite semiconductor and TiO_2 scaffold.

Differently from the injection process, the order of recombination resistance of R_2 observed by EIS (Fig. 4) revealed similar trend of the densities of trap state determined by RDB-PAS in the inset of Fig. 5b and S2. Although the clear mechanism of carrier dynamics in PSC has not been well understood, yet, most of the mechanism in carrier transport has been discussed by borrowing the mechanism in DSCs [71]. In our case of recombination resistance, it is still understandable with the model of trap-detrap process of electron in TiO_2 , which is generally applied to the electron transport mechanism in mesoporous TiO_2 electrode in DSC [70,71]. Since the trap-detrap event occurs more often in mesoporous TiO_2 possessing electron traps located at shallower energy level with respect to CB minimum and fewer density, the frequency of trap-detrap event enhance the electron transport through TiO_2 films and the recombination with oxidant in the electrolyte, such as triiodide in DSC [71]. In perovskite case, the model has not been deeply studied with controlled experiments [75], so that the deeper study of carrier transport model has to be desired to understand the electron transport in TiO_2 films after electron injection in PSCs. In our case of perovskite solar cell with different TiO_2 scaffold, the increase of recombination resistance was observed with TiO_2 possessing lower energy level and higher density of electron traps as determined by RDB-PAS. Therefore, the consistency between DSCs and PSCs may exist as the trend of the recombination rate constant and the frequency of electron trap-detrap event in TiO_2 .

As DSCs and PSCs are typically concerned with low energy level of electron traps and CB, which decrease the quasi-Fermi level, and thus V_{OC} , the low energy levels are not appreciated to increase device performances [70,73]. However we observed the $\{001\}$ facet-dominant anatase TiO_2 possessing lower energy level in CB and trap states even with higher density of state exhibits higher V_{OC} . Similar discrepancies of the quasi-Fermi level (V_{OC}) increase with lowering energy level of CB has been already observed with a few reports of SnO_2 scaffold possessing lower CB energy level [79], Li treatment of TiO_2 lowering CB [72], etc., and consequently the main determinant of quasi-Fermi level in n-type semiconductor has been still unknown in PSCs. In our case, the CB energy level lowered by introducing larger fraction of $\{001\}$ under comparison of the series of $\{001\}$ facet dominant TiO_2 . Because of this fundamental CB property of $\{001\}$ facet dominant TiO_2 , V_{OC} tend to decrease with $\{001\}$ facet dominant TiO_2 as observed in J-V characteristics (Fig. 2 and Table 1). However we have to take another factor of V_{OC} into the account, which is the recombination resistance also contributing to increase V_{OC} . Consequently higher V_{OC} was observed with higher fraction of $\{001\}$ facet with the series of NS TiO_2 , and thus NS74% exhibited the highest V_{OC} possibly due to the highest recombination resistance among series of NS TiO_2 , which was observed by EIS. As the result, the PSCs with NS74% revealed the comparable V_{OC} to that

beam photoacoustic spectroscopy of metal-oxide powders for estimation of could be the ensemble of electron transport property and electron traps and CB with density of state and energy level on the scaffold and possibly the band alignment of the perovskite crystals and TiO_2 with respect to the quasi-Fermi level. As the relatively deeper traps could slow down the recombination kinetics and even increase V_{OC} , the density of electron traps and energy level of CB and trap states controlled by increasing the fraction of $\{001\}$ facet of anatase nanoparticles consequently could be one of important factors to improve the electron injection from the perovskite and also to suppress the recombination in PSCs.

These trends of injection and recombination kinetics affected by the contacted facet were also consistently observed with the trend of photoluminescence (PL) and photoluminescence lifetime (PLLT) under open-circuit [80] and short-circuit configurations [81], in order to confirm the trend of recombination and injection kinetics, respectively (S5). As previous report suggested that the lifetime under open-circuit configuration are directly related to the density of non-radiative recombination arisen from defect-related recombination center, longer lifetime PL indicates the suppression of bimolecular recombination under open-circuit configuration results in higher intensity of PL and thus high V_{OC} in solar cell devices [80]. On the other hand, the quenching rate of PL under short-circuit configuration is also directly related to the electron injection from photo-excited perovskite crystals to n-type semiconductors [81]. The results of the shorter lifetime in PLLT was observed as $\{001\}$ fraction increased, and thus these results support the discussion of electron transfer process at TiO_2 /perovskite interfaces, which can be enhanced by $\{001\}$ facet as mentioned above. However, we still need further study to comprehensively understand the carrier dynamics in order to correlate them, one hand, to the surface properties of mesoporous scaffold, and the other hand, the device characteristics of PSC, as the previous study has pointed out [82].

As consequences, EIS results confirm that the charge transport properties and energetics of CB and trap state below CB are controlled by the anatase $\{001\}$ facet exposed on the mesoporous scaffold in PSC device configurations. Although the EIS analysis is still under debate, we observed sufficiently consistent results with the characteristics of CB and trap density with energy levels by PAS analysis of TiO_2 scaffolds. Therefore we conclude that the higher conversion efficiency observed in J-V characteristics of PSC devices with NS74% (Figs. 2 and 3) are attributed to the fundamental properties of charge transfer process of slower recombination kinetics and first injection due to the energetics at the interfaces, which can be controlled by the fraction of $\{001\}$ facet on mesoporous anatase TiO_2 as the scaffold in PSCs.

4. Conclusion

We focused on the primitive facets of $\{001\}$ and $\{101\}$ on anatase TiO_2 nanoparticles and studied the device characteristics with the variation of the fraction of anatase $\{001\}$ facet on mesoporous scaffold in PSC. We systematically varied the fraction of $\{001\}$ facet of anatase TiO_2 nanoparticles up to ~74% and examined effects of $\{001\}$ facet on device characteristics. The results revealed the highest conversion efficiency with the largest fraction of $\{001\}$ of 74% exposed on anatase TiO_2 mesoporous scaffold. Furthermore, we performed EIS to evaluate the electron transport and capacitance properties with each mesoporous TiO_2 scaffold in the perovskite solar cell device configurations. Based on the conventional interpretations of the EIS, we tried to reveal the correlation of those impedance components to observed device characteristics. The results of PAS based characterization of TiO_2 scaffold revealed the band gap energy and ERDT. The results indicate that the interfacial

charge transport properties at TiO₂/perovskite interface are significantly affected by the fraction of anatase {001} facet on mesoporous TiO₂ scaffold potentially attributed to the nature of surface chemistry and the energetics of CB and density and energy level of electron trap states. We therefore concluded that the {001} facet-dominant anatase TiO₂ scaffold contributes to the higher efficiency of PSC with the enhancement of the electron transfer from perovskite semiconductor to TiO₂ scaffold and the suppression of the charge recombination at the interface of TiO₂/perovskite, and thus result in higher J_{SC} and V_{OC} were proposed to be controllable by the fraction of {001} facet on anatase TiO₂ scaffold. We consequently believe that the clear understanding of the effects of {001} facet dominant anatase TiO₂ on electron transport properties in cells would potentially bring the higher conversion efficiency and long-term stability of PSCs.

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Effects of Energetics with {001} Facet-Dominant Anatase TiO₂ Scaffold on Electron Transport in CH₃NH₃PbI₃ Perovskite Solar Cells

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S1. Preparation of mesoporous titania scaffold and perovskite solar cell devices

S1-1 Hydrothermal synthesis of anatase TiO₂

The conventional hydrothermal synthesis previously reported was applied to synthesize the series of {001} facet-dominant anatase titania nanoparticles. The synthesis procedure typically consists of the precursor solution composed of tetrabutoxytitanium(IV) (Ti(OBu)₄, 25 mL) and aqueous hydrofluoric acid solution (HF, 3 mL) with varying concentrations to change the resulted fraction of {001} facet. The mixed precursor solutions were tightened in a Teflon-lined autoclave container and kept at 180 °C for 24h in an oven. 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) and then rinsing with distilled water until pH 7.0 was achieved in order to remove fluorinated titanium products on titania surface¹⁻³. The washed samples were confirmed that there is no fluorinated compound as the contamination of the surface by XPS analysis, while the spectra are not shown here⁴.

S1-2 Preparation of anatase TiO₂ Paste

Earned titania nanoparticle suspensions in ethanol were then processed to prepare a titania paste for creating mesoporous titania films by adding binders of α -terpineol and ethylcellulose dispersed in ethanol. The mixed suspensions composed of titania (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 sonichone (titanium) followed by ball milling with zirconia beads for 20h. Finally the ethanolic solvent was evaporated by rotary evaporator under 45 °C to earn the 8~10wt% of titania as the stock suspension paste. The titania mesoporous films of each titania were prepared by diluting the stock suspensions of titania paste with a corresponding amount of ethanol and coated on F:SnO₂ covered glass substrates (FTO, TEC-15, Nihon Sheet Glass, Japan) by a spin-coat method followed by annealing at 500 °C for 30min in an oven⁵. The concentrations of the diluted pastes were controlled based on the resulted thickness of the final titania films to earn the identical thickness.

S1-3 Perovskite device construction⁶

The perovskite solar cells (PSCs) were fabricated by constructing layers of compact titania, mesoporous titania, CH₃NH₃PbI₃ perovskite, organic hole transport layer (HTL), and metal counter electrode on a fluorine doped tin-oxide as the transparent conducting oxide glass (FTO, TEC-15, Nippon Sheet Glass Co. Ltd.) by mainly employing the wet coating processes. Firstly, the compact titania layer was deposited by an aerosol spray pyrolysis of titanium diisopropoxide bis(acetylacetonate) solution in isopropanol (75%, Sigma-Aldrich) diluted with 9-equivalent volume of ethanol onto FTO substrates located on a hotplate heated at 500 °C under ambient atmosphere. After cooled to room temperature (~25°C), the substrates were kept in an aqueous solution (0.04M) of titanium tetrachloride (0.09M diluted in HCl, Sigma-Aldrich) for 30min at 70 °C, then washed by distilled water, dried under nitrogen gas, and finally annealed in an oven at 500 °C for 30min. And then the prepared titania paste was spin-coated onto the compact titania. The spin-coating procedure were separately optimized with the top spinning rotation of around 3000-6000rpm in order to achieve almost identical thickness of mesoporous titania layers possessing 280nm $\pm$ 30nm thick. The coated mesoporous titania was sintered in an oven for 30

min at 500 °C. Then the PbI_2 (1.2M, Aldrich) in *N, N'*-dimethylformamid (DMF) solution was spin coated at the top spinning at 6000 rpm for 10 sec and dried in nitrogen ambient. A UV-ozone treatment was performed for 15 min right prior to the PbI_2 deposition to remove the organic contaminants on the titania surface.

After drying the PbI_2 films at 70 °C on a hot plate for 30 min under dried nitrogen atmosphere, the substrate was then transferred into a dry-air chamber. The PbI_2 films were then immersed into an isopropanolic solution of methylammoniumiodide (50 mM) and kept for 20min in order to convert the films to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. The samples were then quickly rinsed with isopropanol and annealed at 70 °C on a hot plate for 30 min under dried air atmosphere right after dried by a spin-drier. After cooling the sample to room temperature ($\sim 25^\circ\text{C}$), a solution to prepare spiro-MeOTAD HTL was spin-coated onto the perovskite films at the top springing at 4000 rpm for 30 sec under dried air ambient; the spiro-MeOTAD solution was composed of 100 mg of spiro-MeOTAD, 40 μL of *tert*-butylpyridine (Sigma-Aldrich), 24.2 μL of lithium bis(trifluoro methanesulfonyl)imide (520 mg/mL in acetonitrile stock solution), and 40 μL of an organo cobalt complex compound (300 mg/mL in acetonitrile stock solution, FK102, Dyesol co., ltd.) in 1 mL of chlorobenzene. And finally the PSC devices were completed by preparing the thermally deposited Au counter electrode (80nm thick) in a vacuum thermal evaporator ($<10^{-6}$ torr).

S2. Characterizations of titania nanoparticles and mesoporous films

S2-1 Evaluation of facet fractions of anatase TiO_2

The synthesized titania nanoparticles dispersed in ethanol by sonication were dropped onto carbon-coated copper grids and dried in vacuum for overnight. The morphologies were observed by field emission scanning electron microscopy (FE-SEM S-5500, Hitachi, Japan) under an acceleration voltage of 5kV.

Based on the ideal decahedral anatase titania crystal indicated in Scheme S2-1^{4, 7-9}, we determined the geometric values of synthesized titania nanoparticles from mean diameter in a and c axis measured in SEM images (Figure S2-1) as summarized in Table S2. According to the assumption of interplane angle between (101) and (001) faces to be $\theta=68.3$ degree^{4, 7-9} we calculated values of d and L geometrically and summed surface areas of {001} and {101} facets, $S_{(001)}$ and $S_{(101)}$, respectively.

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

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

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

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

The fraction of {001} facets were determined from $S_{(001)} / S_{total}$. The volume and weight of single particle were also calculated from these geometric factors with density of anatase titania, 3.9g/cm^3 .

Scheme S2-1 The modeled ideal anatase titania nanoparticle structure used for the calculations of geometrical characteristics.⁷⁻⁹

Figure S2-1 SEM images of as-synthesized series titania nanoparticles.

Table S2 Geometrical factors and estimated fractions of {001} for each titania with compositions in precursor solutions.

TiO ₂	NP	NS 38%	NS 57%	NS 74%
Surfactant concentration ^a / wt%	0	12	27	43
Fraction of reactive facet ^b / %	~5	38	57	74
Diameter (a-axis) ^c / nm	10.8±2.6	16.8±4.7	29.8±7.3	41.8±13.1
Diameter (c-axis) ^c / nm	-	8.8±1.5	8.6±1.9	6.3±1.3
BET Surface Area ^d / m ² · g ⁻¹	111	78	75	77
Porosity ^e / %	0.617±0.084	0.622±0.041	0.634±0.025	0.620±0.037
Roughness Factor ^f / 1μm thick	165.8	115.0	107.1	114.1

^a The concentration exhibits the hydrofluoric acid concentration used for titania nanoparticle synthesis in the hydrothermal reaction (S1). ^b Values were calculated from the observed diameter in *a*- and *c*-axis by applying the ideal decahedral anatase titania crystal shape as described in S2-1⁴. ^c Values were measured for each crystal in *a*- and *c*-axis of at least 100 particles randomly picked up in SEM images. ^d Brunauer-Emmett-Teller (BET) surface area was determined with the annealed mesoporous titania films by applying a multipoint BET method using the nitrogen adsorption-desorption isotherms (Autosorb-1, Yuasa ionics inc., Japan) in the range of relative pressure, $P/P_0 = 0.05 \sim 0.20$, at 77K. ^e The porosity of each film was evaluated by weighing the films and measuring the volume of films with applying the ideal anatase specific weight of 3.9g/cm³. ^f The roughness factor of each film was evaluated by the ratio of internal surface area over projected area, and therefore the internal surface area was determined by the film density and BET surface area in a specific film with a thickness of 1μm.

S2-2 Characterization of anatase TiO_2 mesoporous films

Transmittance spectra of each mesoporous titania scaffold were obtained in the UV-vis region, 300-1000nm, 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. This indicates the optical scattering characteristics of each films were identical. The powder x-ray diffraction (MiniFlex, Rigaku, Japan) was measured with the annealed titania mesoporous films revealing the expected diffraction peaks, which all are attributed to anatase titania with all of samples.

Figure S2-2 (a) XRD and (b) transmission spectra of mesoporous titania films.

S2-3 Photoacoustic spectroscopy (PAS)^{10, 11}

The bare TiO_2 scaffold were examined in terms of electron trap density and band gap by means of reversed double-beam (RDB-) and single-beam (SB-) photoacoustic spectroscopy (PAS), respectively.^{10, 11}

A home-built PAS system was utilized for the measurement of single beam (SB-) and reversed double-beam (RDB-) photoacoustic spectroscopy. A home-made aluminum PAS cell with a quartz window and a microphone (Knowles Electronics SP0103NC3-3 electret condensermicrophone) was used.¹¹ A powder sample (~100 mg) was set in a sample holder in the cell, and ambient-temperature argon flow saturated with methanol vapor was made to flow through the cell for at least 30 min and then the cell was sealed off. The purpose of methanol saturation in the measurement is to capture those positive holes irreversibly and thereby to avoid disappearance of once-trapped electrons through the reaction with positive holes. A monochromatic light beam from a xenon lamp (Spectral Products ASB-XE-175 xenon light source) equipped with a grating monochromator (Spectral Products CM110 1/8m grating monochromator) and an LED beam (Luxeon LXHL-ND98 625-nm light-emitting diode) voltage-modulated (80 Hz) by a function generator (NF Corporation DF1906 digital function generator)

were mixed by a UV quartz combiner light guide (Moritex MWS5-1000S-UV3) and irradiated from the upper side of the sample cell. The PA signal was acquired in lock-in mode (NF Corporation LI5630 digital lock-in amplifier) and averaged at each wavelength of continuous light during scanning from 650 nm to 350 nm with a 5-nm step. In the conventional SB-PAS analysis, PA signal intensity is calibrated with a blank using graphite as a black body to compensate for wavelength-dependent light intensity, but no such calibration is made in RDB-PAS since the signal intensity, corresponding to the total accumulated trapped-electron density, is independent of continuous-light intensity and modulated-light intensity is constant throughout an acquisition. The thus-obtained RDB-PAS spectrum, a plot of total accumulated electron-trap density as a function of photon energy ($E/\text{eV} = 1240/(\text{wavelength}/\text{nm})$) of continuous light, was differentiated from the smaller-energy side to obtain the energy-resolved distribution of electron traps (ERDT) as a function of energy as reference to the valence band maximum (VBM). The absolute density of electron traps was calibrated by comparison with total density of electron traps observed by the photochemical method.¹²

Conventional SB-PA spectra using a single chopped light beam were recorded in the setup of RDB-PAS; the wavelength scanned light from a xenon lamp/monochromator was attenuated and chopped (80 Hz), and the PA signal was detected and averaged. The spectra were calibrated with the spectrum taken for graphite to compensate for wavelength-dependent light intensity. The bandgap of a sample was simply determined by extrapolating the linear part of a rise in the shorter wavelength region; a Tauc plot, which is frequently used for determination of the bandgap, was not used due to the ambiguity of decision of direct/indirect transitions.^{13, 14}

Figure S2-3 (a) Absorption spectra obtained by SB-PAS and (b) trap density determined by RDB-PAS of each TiO₂ mesoporous scaffold exposing {001} facet with fractions of 74 (red), 57 (orange), 38 (light green), and ~5% (green).

S3. Characterizations of perovskite films on TiO₂ scaffold.

The plane SEM images of bare perovskite films on each titania scaffold indicates there is no significant difference. Transmittance spectra of perovskite solar cell devices prepared on each mesoporous titania scaffold were obtained in the UV-vis region, 300-900nm, by a UV-vis spectrometer (JEOL, JSM-7600F) with transmission mode. The transmittance of each films were almost identical in the UV-vis region. This indicates the optical scattering characteristics of each films were identical. The powder x-ray diffraction (MiniFlex, Rigaku, Japan) was measured with the annealed titania mesoporous films revealing the expected diffraction peaks, which all are attributed to anatase titania for all the samples.

Figure S3-1 SEM plane images of bare CH₃NH₃PbI₃ films on each mesoporous titania scaffold.

Figure S3-2 (a) UV-vis transmission and (b) XRD spectra of MAPbI₃ films on each mesoporous titania scaffold.

S4. Evaluation of perovskite solar cell device performances

S4-1 I-V and IPCE measurements

Photovoltaic measurement of the fabricated PSCs was conducted using a solar simulator equipped with a 450 W xenon lamp (model 81172, Oriel) as light exposure and a source-measurement unit (Keithley, model 2612A). The spectrum of the solar simulator and its power were adjusted to 100 mW/cm² at AM 1.5 using a reference Si photodiode. Current-Voltage characteristics were measured after the simulated solar irradiation to estimate the photovoltaic parameters such as short-circuit current density (J_{sc} in mA/cm²), open circuit voltage (V_{oc}), and the fill factor in order to estimate the photoconversion efficiency (η) of the relationship.

$$\eta(\%) = J_{sc}(\text{mA}/\text{cm}^2) \times V_{oc}(\text{V}) \times FF \quad (\text{S4-1})$$

S4-2 IPCE measurements

Incident photon to current conversion efficiency (IPCE) was measured by using a PVE300 (Bentham), with a dual Xenon/quartz halogen light source, measured in DC mode without any bias light. The monochromatic photon flux density was adjusted to 1×10^{16} which 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.

Figure S4-1 Current-voltage characteristics of PSC devices utilizing each mesoporous TiO₂ scaffold layer under solar simulator(AM1.5).

S4-3 Electrochemical impedance spectroscopy

The impedance spectra of each PSC device with different titania scaffold were measured at different DC bias voltages along the working regime of the cells (from short circuit to open circuit conditions) under AM1.5 irradiation. The modulated AC voltage perturbations had amplitude of 20mV and a frequency of 0.4MHz ~ 10mHz range. Although the analyses of EIS taken with PSC are still under debates, we applied a simple model previously reported to extract the resistance and capacitance components of each RC elements based on a general equivalent circuit form the Nyquist Diagram¹⁵

Scheme S4-1 Schematic equivalent circuit models applied to EIS analysis.

Figure S4-2 (a) Examples of Nyquist Diagram for plots under each potential conditions.

S5 Photoluminescence spectroscopy and photoluminescence lifetime

The photoluminescence (PL) spectroscopy and photoluminescence lifetime (PLLT) of each PSC device with different titania scaffold were measured under open-circuit and short-circuit configurations, respectively. The excitation of PL and PLLT were solid state pulse laser diode with the pulse width of ~ 100 psec (2 uJ/cm^2 at 483 nm) configured in the time-correlated single photon counting system (C7990, Hamamatsu photonics, Japan). In the short-circuit case, the each contact for FTO of TiO_2 side and gold counter electrode of solar cell device was connected by a electric wire. Under open-circuit condition, the device after illumination is relaxed with the process of non-radiative and radiative recombination without significant carrier movement. Therefore the radiative recombination typically represents the quality of perovskite crystals and non-radiative recombination represents the defect-related imperfection of either perovskite, titania, or interfaces. These imperfections could behave as the non-radiative recombination centers, and therefore the *quasi*-Fermi level under illumination could potentially decrease due to recombination under working condition of solar cells. V_{OC} thus potentially relate to the radiative recombination lifetime under open-circuit condition. This is regularly discussed in the previous results, although generally papers do not really mention that is under open-circuit conditions including the non-device configuration¹⁶. In the short-circuit condition, most of electron and hole are extracted by the electrodes and recombined as non-radiative process out of cells. Therefore most of carriers are extracted by the electrode under short-circuit condition, and thus the observed radiative recombination occurs only as the recombination loss in perovskite crystals. In case of short-circuit condition, PL as radiative recombination thus are not appreciated for high-efficiency devices, and consequently the shorter component of lifetime, the better device is supposed to have. These context was also discussed in detail in the previous reports¹⁷. They observed the negative correlation between the lifetime and Intensity of PL with photo-current in the local space. Thus the life time under short-circuit condition would potentially represents the injection efficiency of carriers as the previous paper mentioned¹⁷.

Figure S5 (a) PLLT and PL spectra of PSC device with different titania scaffold under short-circuit and open-circuit configurations, respectively.

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