Niobium Doping Effects on TiO$_2$ Mesoscopic Electron Transport Layer-Based Perovskite Solar Cells

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Perovskite solar cells (PSCs) are the most promising candidates as next-generation solar energy conversion systems. To design a highly efficient PSC, understanding electronic properties of mesoporous metal oxides is essential. Herein, we explore the effect of Nb doping of TiO$_2$ on electronic structure and photovoltaic properties of PSCs. Light Nb doping (0.5 and 1.0 at %) increased the optical band gap slightly, but heavy doping (5.0 at %) distinctively decreased it. The relative Fermi level position of the conduction band is similar for the lightly Nb-doped TiO$_2$ (NTO) and the undoped TiO$_2$ whereas that of the heavy doped NTO decreased by as much as –0.3 eV. The light-doped NTO-based PSCs exhibit 10% higher efficiency than PSCs based on undoped TiO$_2$ (from 12.2% to 13.4%) and 52% higher than the PSCs utilizing heavy doped NTO (from 8.8% to 13.4%), which is attributed to fast electron injection/transport and preserved electron lifetime, verified by transient photocurrent decay and impedance studies.

Introduction

Perovskite solar cells (PSCs) based on light-absorbing materials (LAM) consisting of organometallic halides have become a strong challenger for conventional solid-state solar cells owing to cost-efficient processes for fabrication as well as high power conversion efficiencies (PCEs). The record PCE of PSCs has rapidly grown to ~19% [1] since the first report of all-solid-state device structures in 2012 [2].

PSCs have various cell structures, for example, mesoscopic structures [3], meso-superstructures [4], and planar junctions [10] based on the electron transport properties of the perovskite LAMs. In general, mesoscopic device structures are needed for perovskite LAMs which have short (~100 nm) charge diffusion lengths (e.g., CH$_3$NH$_3$PbI$_3$). There have been many studies to match appropriate hole-transport materials (HTMs) with LAMs in mesoscopic devices [5, 6]. However, mesoporous electron transport materials (ETMs) have been less studied in spite of the recent findings that the mesoporous ETM layer critically affects the charge diffusion lengths in the photoelectrode of solar cells and the hysteresis characteristics of the device performance [7, 4]. A high performance and less hysteresis in photovoltaic properties could be obtained by modifying the mesoporous ETM. [8] Recently, metal-oxide-based mesoporous ETMs have been studied with emphasis on modifications of morphology/structure [9], chemical/physical properties of the ETM/LAM interfaces [10], and the electronic band structure [11–13] and the material itself [14, 15]. Those approaches were effective for adjusting electron transport and recombination properties and device stability.

Doping chemistry is one of the most effective methods to modify both the electronic band structures and surface states of a material. Thus far, however, doping effects have not been intensively studied in PSCs, whereas it is well studied in liquid-electrolyte-based dye-sensitized solar cells (DSCs). Especially, divalent substitutions using Y$^{3+}$, Nb$^{5+}$, or Ta$^{5+}$ doping into TiO$_2$ are known to be effective in modifying electrical properties of TiO$_2$ [11, 16, 17]. Among them, Nb$^{5+}$ is regarded as an appropriate n-type dopant that enhances the charge collection properties. In DSCs, several groups demonstrated this effect by adopting a degenerate Nb:TiO$_2$ (NTO) compact layer [18] and a NTO nanoparticles (NPs)-based mesoporous layer [16]. However, previous studies on NTO NPs could not see isolate the pure effect of Nb doping on photovoltaic properties because the NTO NPs had different sizes or different phases at different Nb doping levels [16, 19, 20]. In PSCs, moreover, there are a few reports on the effect of p-type dopants, such as Y$^{3+}$, Al$^{3+}$ [11, 12] but the
effects of n-type dopants, especially Nb$^{5+}$, have not been systematically investigated yet.

Herein, we report the effects of Nb doping of TiO$_2$ NPs on the electronic structure of TiO$_2$ and on the NTO NP-based PSCs performances. Well-crystallized NTO NPs (0, 0.5, 1.0, and 5.0 at% of Nb) were successfully synthesized using a two-step sol–gel (TSSG) method. Electronic band structures of the NTOs were investigated using UV/Vis spectroscopy and valence-band X-ray spectroscopy (XPS). When the NTO NPs were used for mesoporous ETM layers in PSCs, 0.5 at%-doped-NTO (05NTO) showed faster electron transport and longer electron lifetime than undoped TiO$_2$ and 5.0 at%-doped-NTO (50NTO). As a result, PSCs based on 05NTO exhibited higher PCEs than PSCs based on undoped TiO$_2$ (10%) or 50NTO (52%).

Results and Discussion

Characterization of NTO NPs

NTO NPs were successfully synthesized using the TSSG method, which is well described in previous reports (see the Experimental Section for details)\(^{[21,22]}\). The final oxide NPs have a uniform size and high crystallinity as the oxide NPs are grown in a metal hydroxide gel network, which is prepared from a metal-alkoxide precursor solution. In this study, Nb ethoxide as the Nb source was added to the Ti-isopropoxide-based precursor solution. The Nb concentrations ([Nb]/[Ti]) were 0.5 (05NTO), 1.0 (10NTO), and 5.0 at% (50NTO). Transmission electron microscopic (TEM) images of the 05NTO NPs are shown in Figure 1a and b. The NPs are well dispersed and have a mean diameter of ~30 nm. The $d$-spacing obtained from the lattice fringes is 0.36 nm, which corresponds to the (101) plane of anatase. The selected-area electron diffraction (SAED) pattern (Figure 1c) reveals that the 05NTO NPs are well crystallized in the anatase phase without the presence of impurities (such as Nb$_2$O$_5$). Energy-dispersive X-ray spectroscopic (EDS) mapping shows that Nb is not segregated but well dispersed in the TiO$_2$ nanoparticles, indicating successful doping. The 10NTO and 50NTO NPs also do not show Nb agglomeration (Figure S1 in the Supporting Information). Precise Nb concentrations for the NTOs were measured using an electron probe microanalysis (EPMA) system and XPS (Figure S2 and S3 in the Supporting Information). The measured Nb concentration is proportional to the concentration of the initial Nb source for the synthesis. The XPS analysis shows the existence of the Nb$^{5+}$ state in the 05NTO, 10NTO, and 50NTO NPs, implying n-type doping. The Nb concentration calculated using the XPS spectra is consistent with the EPMA results. Figure 2a shows scanning electron microscopic (SEM) images of the NP-based mesoporous films on fluorine-doped tin oxide (FTO) substrates. The films were fabricated through spin-coating of a NP-based paste and subsequent annealing at 500 °C in air. All films made using the 00NTO, 05NTO, 10NTO, and 50NTO NPs had very similar particle size (~32 nm) and porosity (~24%, pore area per total area from the SEM images). The mean particle sizes are plotted in Figure 2b. The particle sizes before and after the annealing process are almost the same. In addition, X-ray diffraction (XRD) patterns of the mesoporous films show only the anatase phase without the presence of any Nb oxides. Therefore, Nb doping was successful owing to a high solubility of Nb in anatase up to ~20%\(^{[23]}\).

Electronic structure and surface defects of the synthesized NTOs were investigated by means of optical absorbance and valence-band XPS analysis. Figure 3a shows the absorbance spectra of the NPs. Interestingly, the absorption edges shift in

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**Figure 1.** Typical TEM images are shown (a) and (b). c) SAED pattern of 05NTO nanoparticles and d) EDS elemental mapping images showing Ti, O, and Nb elements in the NPs.

**Figure 2.** a) Plane-view FESEM images of 00NTO, 05NTO, 10NTO, and 50NTO NP-based mesoporous films, b) average particle size calculated from the FESEM images, and c) XRD patterns of the films. Cross marks and end of error bars represent minimum and maximum values, and the middle line in each box represents the median value. Upper and lower ends of the box represent the third quartile (25%) and first quartile (75%), respectively. Filled squares indicate mean values.
different directions depending on amount of doping; a small blue shift occurred on light doping whereas a distinctive red shift can be observed for heavy doping. The optical band gap energies are evaluated to be 3.23, 3.26, 3.25, and 3.17 eV for 00NTO, 05NTO, 10NTO, and 50NTO, respectively, by fitting the spectra using the equation $\alpha h\nu = A(h\nu-E_g)^m$, where $\alpha$ is the absorption coefficient, $A$ is the constant, $h\nu$ is the incident photon energy, and $E_g$ is the optical band gap energy; $m = 1/2$ for an indirect semiconductor. This phenomenon was observed several times before, but the origin has not been understood clearly yet.\[24, 25\]

Figure 3b shows the valence-band XPS spectrum. The relative position of the valence band maximum (VBM) with regard to the Fermi level ($E_F$) can be determined by linear extrapolation of the spectrum. The extrapolated $x$-axis intercepts of 05NTO and 10NTO are located around that of the undoped TiO$_2$, whereas 50NTO shows a clear shift of the position to a higher binding energy (as much as ~0.24 eV), which indicates that $E_F$ of the 50NTO departs more from the VBM level compared to the other samples. Considering the $E_F$ reduction (~0.06 eV) of 50NTO, it is clear that the $E_F$ of 50NTO is considerably closer to the conduction band minimum (CBM-$E_F$) than that of the undoped TiO$_2$ (as much as ~0.3 eV) whereas the CBM-$E_F$ of the lightly doped NTOs are very similar to the undoped TiO$_2$.

### Photovoltaic properties of NTO-based PSCs

Photovoltaic properties of the NTO-NP-based PSCs (with a 0.14 cm$^2$ metal aperture) were measured under AM 1.5G conditions (100 mW cm$^{-2}$). The photocurrent density–voltage ($J$–$V$) curves of the optimized devices are displayed in Figure 4a; the mean values of the short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and PCE are summarized in Table 1 and Figure 4b. For each doping level, ten devices were tested. All devices show little hysteresis in the $J$–$V$ curves during reverse and forward scans, but the averaged PCEs calculated from those reverse and forward scans are similar to steady-state PCEs (see Figure S4 in the Supporting Information). It is noteworthy that the 05NTO cells exhibit a PCE by increased by 10% compared to the undoped TiO$_2$ cells, owing to high $J_{sc}$, $V_{oc}$, and FF values, whereas the 50NTO cells show significant deterioration of all parameters, leading to a decrease in PCE by 8.8%.

The differences in photovoltaic properties might result from the charge injection or collection properties of the NTO-NP-based mesoporous films because all PSCs have a similar amount of LAM, which can be evidenced by i) similar NP size and porosity of the NP films, ii) similar thickness of LAM/ETM layer (see Figure S5 in the Supporting Information), iii) negligible difference in optical transmittance of the ETM/FTO photoelectrode (see Figure S6 in the Supporting Information).

![Figure 4.](image-url)
mation) and hence iv) almost the same absorption (A) and reflection (R) spectrum of the LAM/ETM/FTO layers (see Figure S6 in the Supporting Information). The light-harvesting efficiency (LHE) of the NTO-based PSCs are compared in Figure 5a by using the absorption and reflection spectrum, and Equation (1):\[LHE = (1 - R) (1 - 10^{-A})\] \[(1)\]

The LHE of the PSCs show almost the same spectrum over the measured wavelength range. However, external quantum efficiency (EQE, that is, incident photon-to-current efficiency) of the PSCs are very different for the undoped (00NTO), lightly doped (05NTO and 10NTO), and highly doped (50NTO) NTO-based PSCs, as shown in Figure 5b. The lightly doped NTO-based PSCs exhibit higher EQE than the other PSCs in the entire wavelength region, which is consistent with the Jsc trend, implying a superior charge injection/collection of the lightly doped NTOs. As the internal quantum efficiency (IQE, that is, absorbed photon-to-current conversion efficiency) excludes light harvesting, it only reflects the charge injection/collection properties. IQE of the PSCs were calculated by using Equation (2):\[IQE(\%) = EQE(\%)/(LHE)(\%)\] \[(2)\]

and the results are plotted in Figure 5c. Clearly, the PSCs based on lightly doped NTOs exhibit IQE considerably higher (~16%) than that of undoped-TiO2-based PSCs in the entire wavelength range, especially at long wavelengths (600–750 nm).

Charge collection of the PSCs was investigated using transient photocurrent/photovoltage decay and impedance analyses, by which electron transport and recombination properties can be estimated. Figure 6 shows electron transport time constants (τc) extracted from photocurrent decay curves under short-circuit conditions. The τc of all devices show typical power-law dependence on the photocurrent density, which is in compliance with the well-known multiple trapping/detrap.

Figure 6. τc of the PSCs as a function of Jsc. For measuring τc, a probe light (535 nm) and bias light (680 nm) were used; undoped NTO and heavily doped NTO were measured using 0.38, 0.147, and 0.045 nW probe light and 14.99, 2.59, and 0.207 mW bias light whereas lightly doped NTO was measured using 0.3, 0.147, and 0.045 nW probe light and 9.99, 2.59, and 0.207 mW bias light. The occurred charge by probe light rapidly decreased, showing first-order exponential decay. The time constant τ was obtained by fitting to the measured data using the relation \[y = y_0 + Ae^{x/\tau}\]. The collected charge induced by the probe laser was maintained below 0.1% of the steady-state charge.

Figure 7 shows the Nyquist plot and electron recombination time constants (τR) extracted from transient photovoltage decay under open-circuit conditions. The radius of the semicircle in the Nyquist plot decreases with increasing dopant concentration, indicating that internal resistance decreases with Nb doping. The radius of the impedance semicircle corresponds to the internal resistance of the photoelectrode including the HTM, light-harvesting materials (LHM), ETM, and transparent conducting oxide (TCO) layers and the interfaces of the layers, although a common, exact interpretation of impedance components has not been established yet. It was suggested in

In general, the increase of m\textsuperscript{2}t (NTO). The Nb doping resulted in contradictory NbTi*. a) Nyquist plot of the PSCs measured at open-circuit conditions. The impedance spectra measured in at% while it (0.5 measurements (Figure 6). b) \(V_{oc}\) of the PSCs as first, creation of one Ti vacancy per four Nb atoms inserted \([1/4 V_{ni}^{4+}\text{ in Eq (3)}]\); second, stoichiometric reduction of Ti\textsuperscript{4+} to Ti\textsuperscript{3+} \([Ti_{ni}^{3+}\text{ in Eq (4)}]\); and third, Nb\textsuperscript{5+} to Nb\textsuperscript{4+} per one Nb atom inserted \([Nb_{ni}^{4+}\text{ in Eq (5)}]\) as follows expressed in the classical Kröger–Vink notation, respectively: \[1/2 Nb_{2}O_{3} + Ti_{ni}^{x} \rightarrow Nb_{ni}^{x-} + 1/4V_{ni}^{4+} + TiO_{2} + 1/4 O_{2} \text{ (3)} \]
\[1/2 Nb_{2}O_{3} + Ti_{ni}^{x} \rightarrow Nb_{ni}^{x-} + Ti_{ni}^{3+} + 5/4 O_{2} \text{ (4)} \]
\[NbO_{2} + Ti_{ni}^{x} \rightarrow Nb_{ni}^{x-} + TiO_{2} \text{ (5)} \]

The defect type is affected by the synthesis conditions, such as \(Ti\text{ partial pressure, temperature, the Nb concentration, and the energy cost for creating such defects. In our work, the dominant factor determining the type of defects is only the doping level, as the NTOs were synthesized following the exactly same route except for changing the amount of Nb source in the precursor. The case presented in Equation (5) can be excluded, as the XPS spectra (Figure S3 in the Supporting Information) show only the presence of Nb\textsuperscript{5+} in our NTO NPs. At a low doping level Equation (3) is likely preferred because cations tend to remain in their higher oxidation states whereas Equation (4) mainly takes place at high doping levels. Thus, the type of defects changes from a cation vacancy to Ti\textsuperscript{3+} defects on increasing the Nb doping level, which is evidenced by the appearance of Ti\textsuperscript{3+} peak in the XPS spectrum for 50NTO (Figure S7 in the Supporting Information). It was suggested that the oxygen vacancies at the surface of NPs could be reduced by light Nb doping because the Nb\textsuperscript{5+} at the surface site attracts additional oxygen atoms. On the other hand, the Ti\textsuperscript{3+} defect are well known to be accompanied by oxygen vacancies; hence, the concentration of oxygen vacancies can increase on increasing the doping level over a critical point. Considering that the valence band of NTO is dominantly affected by the O2p orbital oxygen vacancies are likely to be responsible for the electronic band change of the NTOs. In this point of view, the high \(V_{oc}\) and the fast electron transport of the lightly doped NTO can be attributed to the reduced amount of oxygen vacancies at the NP surface, which results in a decrease in the electron concentration at the surface. On the other hand, the high oxygen vacancy–Ti\textsuperscript{3+} defect concentration of the heavily doped NTO might reduce the \(V_{oc}\) and the electron life time, as oxygen vacancy–Ti\textsuperscript{3+} is a well known recombination center in mesoscopic solar cells. In addition, these defects might act as scattering centers, which slows down electron transport.\]

Conclusions
We studied the effect of Nb doping of anatase nanoparticles (NPs) on the electronic band structure of TiO\(_2\) and on the photovoltaic properties of perovskite solar cells (PSCs) based on Nb-doped TiO\(_2\) (NTO). The Nb doping resulted in contradictory effects on the electronic structure and photovoltaic properties depending on the doping level. Lightly doped NTO NPs exhibit band-gap (\(E_g\)) and Fermi-level energies (\(E_F\)) similar to undoped TiO\(_2\) NPs and improved electron injection/transport properties when used in PSCs. On the other hand, heavy doping reduces \(E_F\) resulting in an \(E_g\) closer to the conduction band minimum (CBM), and retards the electron injection/transport of PSCs. This contrasting result was attributed to the generation of different defect types depending on the doping level. This result can inspire the design of appropriate n-type electron transport materials (ETMs) of PSCs.

Experimental Section
Synthesis of the NTO NPs
A stock solution of Nb-doped Ti\textsuperscript{3+} (0.5 m) was prepared by mixing titanium isoproxide (TTIP; 97%, Sigma–Aldrich), 2 m niobium(V)
ethoxide, and triethanolamine (TEOA, 98%, Sigma–Aldrich) at a suitable ratio ranging from 1:0.2 to 0.95:0.05:2, followed by the addition of distilled water. Afterwards, the prepared stock solution (pH = 9.3) was mixed with HClO and 0.3 M H2SO4 and NTO film was spin-coated onto the FTO/c-TiO2 film. The synthesized TiO2 NPs were washed using the same process reported in our previous study.[31] The TiO2 paste using the prepared NPs was prepared by modifying the method reported by S. Ito et al.[32]

**Fabrication of the PSCs using the NTO NPs**

The solar cells were fabricated on FTO substrates (TEC15, 15 Ω/sq, Pilkington), which were washed for 15 min each with acetone, deionized water, and ethyl alcohol in an ultrasonic bath. A compact TiO2 (c-TiO2) layer was spin-coated on an FTO substrate at 3000 rpm for 30 s using a 0.15 mm and 0.3 mm titanium disopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Aldrich) solution in 1-butanol (99.8%, Aldrich), which was heated at 125°C for 5 min, respectively, then annealed at 50°C for 30 min. The FTO/c-TiO2 substrate was immersed in 0.04 mM aqueous TIOCl solution at 60°C for 1 h. After washing with deionized water and drying, the substrate was annealed at 50°C for 30 min. Then, a 240–260 nm-thick mesoporous TiO2 and NTO film was spin-coated onto the FTO/c-TiO2 substrate using lab-made pastes and calcining at 500°C for 1 h in air to remove organic components. The synthesis of the CH3NH3PbI3 (MAI) and CH3NH3PbI3 perovskite light absorber layer were prepared by using a modified solvent engineering reported elsewhere.[6] The detailed process was as follows. The prepared CH3NH3PbI3 solution (MAI/CH3NH3PbI3 = 1:1 molar ratio, 43 wt% in a mixture of γ-butylrolylate (GLB) and dimethyl sulfoxide (DMSO) (7:3 v/v) at 60°C for 12 h) was spin-coated at 1000 and 5000 rpm for 10 and 30 s, respectively. For the second spin-coating step (5000 rpm), the toluene was drop-coated on the substrate (around 2×2 cm²) in a glove box.

The substrate was dried on a hot plate at 120°C for 10 min. Subsequently, 40 μL of a hole transport layer (56 mg spiro-MeOTAD, 8.4 μL 4-tert-butylypyridine, and 36.2 μL bis(trifluoromethane)sulfonamide lithium salt (Li-TFSI) solution (77 mg in 0.5 mL acetonitrile) was deposited by thermal evaporation at -10⁻⁶ torr using a shadow mask.

**Characterization**

The crystal structures of anatase and NTO nanoparticles were characterized using an X-ray diffractionometer (New DB-Advance, Bruker Miller Co.). The morphologies and microstructures of the prepared TiO2 nanoparticles and the cross-sectional structure and thickness of the solar cells were investigated using a field-emission scanning electron microscopy (FESEM, JSM-7600F, JEOL). To analyze the morphology and crystal structure of anatase and NTO, high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL) was used. Energy-dispersive X-ray spectroscopy (EDS) images of NTO were also obtained using the same microscope. The absorbance and reflectance of various TiO2 powders dispersed in distilled H2O and TiO2 and perovskite/TiO2 films were measured by means of ultraviolet-visible light (UV/Vis) spectroscopy (Cary 5000, Agilent). The chemical states of Nb and valence-band position in TiO2 and NTO nanoparticles were analyzed using normal and valence-band-mode X-ray photoelectron spectroscopy (XPS, Sigma Probe, ThermovG, UK). All XPS peaks were calibrated with respect to the C1s level at 284.5 eV. The current–voltage characteristics of the solar cells were measured under solar-simulated light (Newport Oriel Solar 3 A Class AAA, 64023 A) by using a potentiostat (CHI 600D, CH Instruments). The AM 1.5G sun light (100 mW cm⁻²) was calibrated using a standard Si-solar cell (Oriel, VLSI standards). Impedance spectroscopy was carried out at open-circuit conditions by applying an AC amplitude signal of 5 mV and frequencies ranging from 10 mHz to 2 MHz using the same potentiostat at 1 sun light illumination. External quantum efficiency (EQE) was measured using an EQE system (PV Measurements Inc.). The source light for generating the monochromatic beam was a 75 W Xe lamp (USHIO, Japan). EQE data acquisition was carried out at DC mode. Transient photocurrent measurements were performed using a small light perturbation, where probe light was incident over the steady-state charge induced by a bias light. The detailed measurement conditions were the same previously reported by Son et al.[33]


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Supporting Information

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Figure S1. EDS elemental mapping images showing Ti, O, and Nb elements in the a) 10NTO NPs, and b) 50NTO NPs, respectively.
Figure S2. Measured Nb concentration using EPMA, as a function of added Nb concentration in the precursor solution.
Figure S3. XPS spectra of the NTO samples from 204 to 212 eV of binding energy which corresponds to the Nb 3d core level.
Figure S4. (a) J-V curves of the 05NTO NPs-based perovskite solar cell measured with the forward (green) and reverse (red) scan directions. The black curve shows the average of two J-V curve, and blue PCE curve is calculated from the average J-V curves. (b) The steady state PCE, as a function of time, obtained with applying 0.8 V of bias voltage that is similar to maximum power output potential.
Figure S5. Cross-sectional SEM images of the NTO NPs-based perovskite solar cells.
Figure S6. a) Transmittance spectra of the ETM (NTO)/FTO films, and b) Absorbance and reflectance spectra of the LHM/ETM/FTO films.
Figure S7. XPS spectra of the NTO samples from 456 to 467.5 eV of binding energy which corresponds to the Ti 2p core level.