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Photovoltaic performance of perovskite-sensitized mesoscopic solar cells could be effectively enhanced by employing Nb-doped TiO$_2$ compact layer, in comparison to device using pristine TiO$_2$ compact layer.
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ABSTRACT

Perovskite solar cells are one of the most promising alternatives to conventional photovoltaic devices, and extensive studies are focused on device optimization to further improve their performance. A compact layer of TiO$_2$ is generally used in perovskite solar cells to block holes from reaching the fluorine doped tin oxide electrode. In this contribution, we engineered TiO$_2$ compact layer by Nb-doping, which led to solar cells with a power conversion efficiency (PCE) of 10.26%, which was obviously higher than that of the devices with the same configuration but using a pristine TiO$_2$ compact layer (PCE = 9.22%). The enhancement of the device performance was attributed to the decreased selective contact resistance and increased charge recombination resistance resulting from Nb-doping, which was revealed by the impedance spectroscopy measurements. The developed strategy highlights the importance of interface optimization for perovskite solar cells.

As one of the most promising alternatives to conventional photovoltaic devices, perovskite solar cell has been intensively investigated in the past few years [1-6]. Great progress has been made in the device fabrication and significant improvement of device performance has been achieved, as evidenced by the recently reported efficiency of 19.3%, in comparison with 3.81%, the efficiency of the first perovskite solar cell reported in 2009. [7, 8] Moreover, perovskite solar cells with various configurations have also been demonstrated. A hole-blocking layer, in most cases, a compact layer of TiO$_2$ is generally used between the FTO conducting substrate and the mesoscopic scaffold and/or perovskite layer to prevent the holes in perovskite or hole-transporting
layer from reaching the FTO substrate [8-15]. The importance of the hole-blocking layer in both perovskite solar cells and its predecessor, the solid state dye-sensitized solar cells has been well acknowledged [16]. Nevertheless, engineering the hole-blocking layer to improve the device performance has been rarely reported. In this work, we report the Nb-doped TiO$_2$ compact layer and its application in perovskite solar cells with mesoscopic TiO$_2$ layer as the scaffold of perovskite. The devices with the Nb-doped TiO$_2$ compact layer could reach a power conversion efficiency (PCE) of 10.26%, which was obviously improved as compared to those devices using a pristine TiO$_2$ compact layer with an efficiency of 9.22%.

Both the pristine and Nb-doped TiO$_2$ compact layers were prepared via spray pyrolysis, and the details are shown in the electronic supplementary material (ESM). The compact layers were first characterized with a field emission scanning electron microscope (FESEM), and typical images are presented in Figure 1. Both pristine and Nb-doped compact layers are smooth and homogeneous, which are significantly different from the morphology of FTO (Fig. S1a, b). The compact layers are formed by the stacking of nanoparticles with the size of a few tens of nanometers (Fig. S1c, d). No discernible difference in morphology between the pristine and Nb-doped compact layers was observed. Only a peak corresponding to 101 reflection of anatase besides reflections of FTO was observed in XRD patterns of both pristine and Nb-doped TiO$_2$ coated FTO substrates (Fig. S2). X-ray photoelectron spectra (XPS) were recorded to investigate the chemical composition of the samples and chemical states of the constituent elements. As revealed by the spectra presented in Figure 1, the binding energies of Ti 2p detected in both pristine and Nb-doped samples are characteristic for Ti$^{4+}$, and no signals of Ti$^{3+}$ and Ti$^{2+}$ are identified in both samples [17, 18]. In addition, the core level spectrum of Nb 3d was obtained from the Nb-doped film (Fig. 1e). Two peaks with binding energies of $207.38 \pm 0.2$ eV and $210.11 \pm 0.2$ eV are detected, which are characteristics for 3d$_{5/2}$ and 3d$_{3/2}$ components of Nb$^{5+}$, respectively [17, 18]. The atomic concentration of Nb element in the doped compact layer was estimated to be $\sim 3.6\%$ using XPS. These results confirmed that Nb was indeed doped into TiO$_2$ compact layer prepared in this study.

![Figure 1](image_url) **Figure 1** SEM images of TiO$_2$ (a) and Nb-doped TiO$_2$ (b) compact layers; XPS core level spectra of Ti 2p (c) for TiO$_2$ compact layer, and XPS core level spectra of Ti 2p (d) and Nb 3d (e) for Nb-doped TiO$_2$ compact layer.
An ideal hole-blocking layer should block the backward transport of electrons from FTO to light-harvesting materials and hole-transporting materials efficiently, on the other hand, hinder the forward transport of electrons from light-harvesting materials to FTO least. Therefore, the rectifying property of a compact layer can give important information on its performance as a hole-blocking layer [19]. To investigate the rectifying behavior of the pristine and Nb-doped compact layers, we fabricated simple devices with the structure of FTO/compact layer/spiro-MeOTAD/Au, where metal Au was used as contact electrode [19-21].

![Figure 2](image_url)

**Figure 2** (a) Current-voltage curves of devices with different compact layers (CL) fabricated using different spraying cycles, open shapes: TiO₂ CL, solid shapes: Nb-doped TiO₂ CL. The positive potential represents that FTO substrate is positively biased, and the current flowing from FTO to spiro-MeOTAD is labeled as positive; (b) Chemical capacitance of blank FTO electrode, TiO₂ CL and Nb-doped TiO₂ CL electrode, measured in liquid electrolyte containing I⁻/I₃⁻ redox couple.

The potential between the two electrodes was continuously increased from -1 V to +1 V [19-21]. The thicknesses of the compact layer were controlled by changing the number of deposition cycles. The typical current-voltage curves of the different devices measured in dark are shown in Fig. 2a. In the case of devices with two cycles of deposition, a linear J-V relationship complying with Ohm’s law was observed, which is similar to that observed for the devices without compact layer (not shown), indicating that no Schottky contact was formed. We speculate that continuous compact layer was not formed after only two cycles of deposition. Furthermore, the resistance of the device with TiO₂ compact layer was slightly larger than that of the device with Nb-doped TiO₂ compact layer, indicating that Nb-doping improved the conductivity of the compact layer. After six spray pyrolysis cycles, the deposited thin film showed significant rectification characteristics. Further increasing the spraying cycles to eight resulted in thin films showing a better blocking effect on the backward electron transport from FTO to spiro-MeOTAD, as evidenced by the lower current density in the third quadrant of Fig. 2a. On the other hand, more spraying cycles also led to thicker films, which are able to hinder the forward transport of electrons more effectively. Eight spraying cycles were thus taken as the optimum preparation parameters in subsequent fabrication of perovskite solar cells. It is noteworthy that Nb-doped compact layer of 8 spraying cycles carries a slightly higher forward and lower backward current in comparison with its pristine counterpart. This implies that Nb-doping results in a slightly improved rectifying property, which will benefit the device performance. The improved rectifying property of Nb-doped compact layer could be explained as follows: Nb-doping is able to increase the carrier (electron) density, and subsequently, the Fermi level of TiO₂ [16]. Therefore, a narrower but higher Schottky barrier is resulted as compared to that in the case of pristine TiO₂. Such a higher Schottky barrier is able to block the backward electron transport more efficiently and the narrower barrier should benefit the forward electron flow. The effect of Nb-doping on the optical transmittance of the compact layers was investigated using UV-Vis spectroscopy. Two types of compact layers presented similar transmittance within the wavelength range from 300 to 850 nm (see Fig. S3).
The electrochemical properties of compact layers were further investigated using electrochemical impedance spectra measured in a three-electrode system with a liquid electrolyte [22, 23]. The chemical capacitances, fitted using the corresponding equivalent circuit [23], of each electrode are displayed in Figure 2b. The chemical capacitance measures the capability of a system to accept or release additional electrons due to the variation of its Fermi level. It was found that the capacitance of blank FTO electrode was independent of the applied bias. However, the capacitance increased exponentially at high applied bias for both pristine and Nb-doped TiO₂ compact layer, indicating that electrons could be accumulated in both films. Furthermore, a significantly higher chemical capacitance was observed within the whole range of applied bias for the Nb-doped TiO₂ layer in comparison to pristine TiO₂ layer. Since the thicknesses of both layers are very close to each other, the higher chemical capacitance observed for Nb-doped film implies the higher density of states than that in the pristine TiO₂ layer, which should facilitate the electron injection from the perovskite to compact layers.

The devices without compact layer, with pristine and Nb-doped TiO₂ compact layers, respectively, were fabricated using the similar process and parameters. The details of device fabrication were given in the supporting information. The current-voltage (J-V) characteristics were measured in dark and under simulated solar illumination (AM 1.5G, 100 mW cm⁻²). The J-V curves of the champion cells of each group are shown in Fig. 3a, and device performance parameters are summarized in Table 1. The devices without compact layer presented the lowest PCE of 3.58%, with an open-circuit voltage (Vₖ) of 0.845 V, a short-circuit photocurrent density (Jₑ) of 9.38 mA cm⁻² and a fill factor (FF) of 0.452. After incorporating pristine TiO₂ compact layers into the devices, PCE, Vₖ, Jₑ and FF increased dramatically to 0.869 V, 17.45 mA cm⁻², 0.608 and 9.22%, respectively. The corresponding parameters for the cells with an Nb-doped compact layer are 0.880 V (Vₖ), 18.08 mA cm⁻² (Jₑ), 0.645 (FF) and 10.26% (PCE), respectively. In comparison with the device applying a pristine TiO₂ compact layer, the device with an Nb-doped compact layer exhibited an enhancement of ~11% in photovoltaic efficiency.

Figure 3 Photocurrent-voltage characteristic curves (a) and incident photo-to-electron conversion efficiency (IPCE) spectrum (b) of perovskite-sensitized solar cells with TiO₂ (solid triangles) and Nb-doped TiO₂ (solid circles) compact layer; (c) Recombination resistance (Rₑ) and selective contact resistance (Rₛ) of perovskite-sensitized solar cells with TiO₂ (solid triangles) and Nb-TiO₂ (solid circles) compact layer, extracted from impedance spectra measured under illumination with applied bias.
forward bias
To illustrate the consistency of the fabrication process, 15 devices were fabricated for each kind of compact layer using the same process and parameters. Photovoltaic parameters of these devices are shown in Fig. S4 and the averages over 15 devices of each group together with the corresponding standard deviations are summarized in Table 1. Devices of each group exhibited consistent photovoltaic performance, as evidenced by the rather small standard deviations of performance parameters. The averaged photovoltaic efficiency of the devices applying Nb-doped compact layers is 9.64% whereas the devices with pristine compact layers show an averaged efficiency of 8.72%. Since the difference in averaged efficiency is bigger than three times the standard deviation, the enhancement of photovoltaic efficiency caused by Nb-doping is statistically significant [24].

The dark current-voltage characteristic curves of various devices were also measured to investigate the blocking effect of pristine and Nb-doped compact layers [25]. As shown in Fig. 3a, the dark current was significantly suppressed by applying a TiO₂: compact layer in the perovskite solar cell, and the onset of the dark current was shifted to higher applied potential by more than one hundred millivolts. Nb-doping further improved the blocking performance, as evidenced by the lower dark current and the onset at a higher bias observed for the Nb-doped compact layer in comparison with those of the pristine one. The lower dark current implies less backward transport of electrons from FTO to perovskite and/or hole-transporting layer, and less hole-electron recombination. Therefore, an improvement of J_{sc} and V_{oc} is expected. Indeed, as shown in Figure 3a and Table 1, the solar cells applying Nb-doped compact layers exhibited slightly increased J_{sc} and V_{oc}. Furthermore, the enhancement in J_{sc} is verified by the incident photo-to-electron conversion efficiency (IPCE) spectra. The IPCE spectra of devices with various compact layers are shown in Fig. 3b. An improvement within the wavelength range from 400 to 600 nm is observed for the Nb-doped device. Furthermore, short-circuit currents calculated from the IPCE spectra are well consistent with the values obtained from J-V curves, which are listed in Table 1. Electrochemical impedance spectroscopy (EIS) has been extensively utilized for the characterization of liquid-state, solid-state dye-sensitized solar cells and perovskite-sensitized solar cells to gain essential information on the internal electrical processes and analyze the associated parameters [22, 26-31]. EIS was consequently employed to investigate the effect of Nb-doping of TiO₂: compact layer on the photovoltaic performance of devices. The spectra of various devices were measured under light illumination at different applied biases [22, 26, 27]. Typical Nyquist plots are shown in Fig. S5a and S5b, while the corresponding equivalent circuit is presented in Fig. S5c [22, 26]. The fitting results of selective contact resistance (R_{sc}) and recombination resistance (R_{rec}) are depicted in Fig. 3c. The series resistance R_s which is mainly attributed to FTO substrate and wires is nearly constant for various devices with a typical value of ~24 Ω. R_{sc} of both types of devices varied slightly with the applied bias (inset of Fig. 3c). In the whole range of applied bias, a slight decrease of R_{sc} resulting from Nb-doping was observed. On the contrary, R_{sc} of the device was improved due to Nb-doping. The improved R_{sc} implies less hole-electron recombination in the device while the decreased R_{sc} indicates more efficient forward carrier transport. The results obtained from EIS data measured on complete devices are in good agreement with rectifying properties observed for both kinds of compact layers. The R_s and R_{sc} will contribute to the total series resistances (R_{series}) of the device [25]. With the doping treatment on the compact layer, the R_{series} of device decreases, which results in improved fill factors as shown in Table 1. These results are in a good agreement with the previously reported results [21, 25]. In addition, the increase in R_{rec} could lead to higher V_{oc} for Nb-doped compact layer based devices. The doping also yielded reduced R_{sc} and R_{series} together with increased R_{rec}, which led to improved photovoltaic parameters, yielding an enhancement in efficiency for Nb-doped compact layer based devices.
In conclusion, Nb-doped TiO$_2$ compact layers were prepared and applied as hole-blocking layers in perovskite-sensitized solar cells. Investigations on rectifying properties revealed that Nb-doping improved not only the blocking effect but also the forward electron transport. Devices with pristine and Nb-doped TiO$_2$ compact layers are also investigated with electrochemical impedance spectroscopy. It was found that Nb-doping of compact layers resulted in improved $R_{sc}$ and decreased $R_{oc}$ of the device, confirming the results obtained from investigations on rectifying properties. Accordingly, an obvious enhancement on photovoltaic efficiency was observed for the devices applying Nb-doped compact layers in comparison with the ones with pristine compact layers. These results show that modification of the compact layer is an understudied avenue where improvements in perovskite solar cells can be achieved.

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Electronic Supplementary Material: Supplementary material (Experimental methods, FESEM images and UV-Vis spectra of FTO, pristine and Nb-doped TiO$_2$ compact layers, photovoltaic performance of perovskite-sensitized solar cells, Nyquist plots of electrochemical impedance spectra of perovskite-sensitized solar cells) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-****.****.

References


Electronic Supplementary Material

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EXPERIMENTAL METHODS

Device fabrication
Fluorine-doped SnO$_2$ (FTO) substrate was firstly etched using Zn powder and HCl (2 M) to form the desired electrode patterns (15 mm ×10 mm). The resultant FTO substrates were ultrasonically cleaned with detergent, deionized water, acetone, ethanol and 2-propanol, respectively. TiO$_2$ compact layer was then deposited on the cleaned FTO substrate by spraying 0.2 M Ti(i-OPr)$_2$(acac)$_2$ at 450 °C. In the case of the Nb-doped TiO$_2$ compact layer, 0.01M Niobium (V) ethoxide was added into the Ti$^{4+}$ precursor solution. Prior to spraying, the solution was ultrasonically mixed for 30 min. The thickness of the compact layers was controlled by changing the number of spray cycles. The mesoporous TiO$_2$ was spin-coated on the surface of the compact layer using the commercial TiO$_2$ paste (Solaronix T/SP) with a diluted concentration. These electrodes were sintered at 125 °C for 10 min, 325 °C for 15 min, 375°C for 15 min, 450 °C for 20 min and 500 °C for 15 min, respectively. The thickness of mesoporous TiO$_2$ was ~450 nm. The PbI$_2$ (Sigma-Aldrich) solution in DMF was dropped on the mesoporous film, and then spin-coated at 5500 rpm for 30 s in a dry Ar box. The film was then dried at 75 °C for 30 min. The film was finally immersed in the CH$_3$NH$_3$I isopropanol solution (10 mg mL$^{-1}$) for 20 s. After that, it was heated at 75 °C for 30 min to form perovskite-sensitized TiO$_2$ electrode. The hole transferring layer was prepared by spin-coating a solution containing 72.3 mg Spiro-MeOTAD, 28.8 µl 4-tert-butylpyridine and 0.06 M lithium bis(trifluoromethylsulfonyl)imide per ml of chlorobenzene on the top of perovskite layer at 4000 rpm for 45s. Finally, Au contact electrode (~80 nm) was deposited on the HTL using thermal evaporation at a pressure of 2 × 10$^{-6}$ mbar.

Characterization
The morphology of the compact layers was observed under field emission scanning electron microscope (FESEM, Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) measurements were conducted with an ESCA Lab250xi spectrometer using Al Kα (1486.6 eV) irradiation as X-ray source. All the spectra were calibrated to the binding energy of the adventitious C1s peak at 284.8 eV. The optical transmittance of the blank FTO, TiO$_2$ and Nb-doped TiO$_2$ compact layer on FTO substrate was measured by using a UV-Vis spectrophotometer (Model Hitachi U3010, Japan). The rectifying behaviors of compact layer were detected using CHI 660D workstation at scanning range from -1.0 V to 1.0 V with a scanning rate of 0.075 V s$^{-1}$. The photocurrent-voltage (J-V) measurements of perovskite-sensitized solar cells were recorded by a Keithley 2420.
source meter with a solar simulator (Oriel Newport, 150 W, AM 1.5) as the light source. The J-V curves were measured by reverse scan (forward bias (1.1V) to short circuit (0V)). The light intensity was calibrated using a Si reference cell (Oriel Newport PN91150V). IPCE measurements of the devices were performed using a 300 W xenon lamp (Newport 66902), a lock-in amplifier (Newport Merlin digital 70140) and a monochromator (Cornerstone CS260). Electrochemical impedance spectra were recorded using a Zahner workstation (Zennium IM6, Germany). Impedance spectroscopy was performed in a three-electrode cell with the blank FTO or different compact layer as the working electrode, the Ag/AgCl and Pt wire as the reference electrode and counter electrode, respectively. I$_3$/I$^-$$^2$ redox couple was dissolved in anhydrous acetonitrile and used as the electrolyte (0.5 mol L$^{-1}$ LiI, 0.05 mol L$^{-1}$ I$_2$). The impedance characterization was performed at negative potential in the range of 0 to -1.0 V with the amplitude of the AC signal of 10 mV and the frequency ranging between 10 MHz and 0.1 Hz. The impedance measurements of perovskite-sensitized solar cells were recorded at an applied DC potential bias with a sinusoidal AC potential perturbation of 20 mV in a frequency range of 2 MHz to 0.05 Hz. The applied DC potential increased from 0 to 0.8 V with a step of 0.1 V. The resultant impedance spectrum was analyzed using the ZView software (Scribner Associates Inc.) and the corresponding equivalent circuit. All the measurements were performed under ambient conditions.

![Figure S1](image)

**Figure S1.** SEM images of blank FTO substrate (a: low magnification; b: high magnification), TiO$_2$ (c) and Nb-doped TiO$_2$ (d) compact layers (high magnification) after 8 spray cycles.
Figure S2. XRD patterns of the blank FTO substrate, as-prepared TiO$_2$ and Nb-doped TiO$_2$ compact layers; * indicates 101 reflection of anatase.

Figure S3. UV-Vis transmittance of blank FTO, TiO$_2$ and Nb-TiO$_2$ compact layer on FTO substrate
Figure S4. Photovoltaic performance of 15 perovskite-sensitized solar cells with TiO$_2$ compact layer (CL) and Nb-doped TiO$_2$ CL, respectively; $V_{oc}$: open-circuit voltage, $J_{sc}$: short-circuit photocurrent density, FF: fill factor, PCE: power conversion efficiency.
Figure S5. Nyquist plots of perovskite-sensitized solar cells with TiO$_2$ compact layer (a) and Nb-doped TiO$_2$ compact layer (b); Symbols represent the experimental data and solid lines are fitted curves; (c) the equivalent circuit used in the study.

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