Low-temperature processed compact layer for perovskite solar cells with negligible hysteresis

Liang Wang, Fenjing Liu, Tianjun Liu, Xiaoyong Cai, Gongtang Wang, Tingli Ma, Chao Jiang

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Hybrid organic/inorganic perovskite solar cells (PVSCs) are promising alternatives to traditional photovoltaic devices because of their low cost, high power conversion efficiency, and simple production process. Therefore, achieving a low-temperature and high-efficiency procedure is necessary to realize the large-scale production of PVSCs. This study developed a facile low-temperature process (70 °C) for the synthesis of anatase TiO2 thin films on the FTO substrate through an in situ growth method. The as-synthesized anatase TiO2 thin films were applied on efficient compact layers of all low-temperature (<100 °C)-processed PVSCs. Under optimization, the achieved low-temperature PVSC device exhibited a champion conversion efficiency of up to 10.33%, with excellent repeatability and negligible hysteresis. Results revealed that fast electron extraction and transfer between perovskite and TiO2 films and effective suppression of charge recombination are the main attributes for the excellent performance of the PVSC device. This work provides a new alternative to achieve low-temperature and high-efficiency photovoltaic devices.

1. Introduction

In recent years, hybrid organic/inorganic perovskite solar cells (PVSCs) are promising alternatives to traditional photovoltaic devices because of their high power conversion efficiency (PCE), low cost, simple preparation procedure, light-weight, and flexibility. From 2009 to 2016, efforts on each part of PVSCs improved the PCE from 3.8% to 20.8% [1–9]. Therefore, PVSCs show a brilliant application prospect for future clean energy supply. In general, a PVSC is composed of a compact layer (CL, e.g., TiO2, ZnO, SnO2, and PCBM) and/or a mesoporous layer (e.g., TiO2, ZnO, and Al2O3) with deposited perovskite as the photodetectrode, 2,2′,7,7′-tetakis(N,N-di-p-methoxy-phenyl-amine) -9,9-pyridinfluorene (spiro-OMeTAD) as the hole-transport layer (HTM), and thermally evaporated Au or Ag as the back electrode. To improve the photovoltaic performance and stability of PVSCs, extensive studies concerning constituent parts, new configurations, and relevant mechanisms have been conducted [10–18]. As an indispensable part of PVSCs, the CL is crucial for the photovoltaic performance and future production of the device.

The CL, namely, electron collection or hole-block layer, is mainly responsible for the high-efficiency electron collection/transport and a suppressing recombination. High-quality CL is the prerequisite for high-efficiency PVSCs. Many materials, such as TiO2, TiO2/graphene, ZnO, ZnO/Al, SnO2, WOx, and PCBM, have been used to prepare the CL [19–31]. At present, the best PCE is realized by TiO2 CL just as that in dye-sensitized solar cells [32]. In general, for achieving high-quality CL, a high-temperature treatment process is required to eliminate organic templates or additives and enhance its crystallization and interconnection. However, the high-temperature preparation generates a high production cost and is unsuitable for flexible devices. Therefore, low-temperature CL preparation is highly anticipated by optimizing preparation technology or searching appropriate new alternative materials. Several methods have been developed and applied to synthesize PVSCs. TiO2, ZnO, SnO2, and WOx materials synthesized using a...
low-temperature process display superior PCEs [19,20,33–35]. To date, however, the Cl of TiO2 is still a major choice for obtaining high-efficiency PVSCs.

In the present work, anatase TiO2 thin films were successfully synthesized through the optimal in situ growth of TiF4 at 70 °C on the FTO substrate. The corresponding assembled PVSCs under 100 °C exhibited an average PCE of 9%. Especially, the champion efficiency of the devices was up to 10.33% with excellent repeatability and negligible hysteresis. Fast electron extraction and transfer between perovskite and TiO2 films and effective suppression of charge recombination are the main factors contributing to excellent performance. The successful introduction of anatase TiO2 into PVSCs also gives a chance for broadening absorption spectra by combining near-IR dyes. It paves a new way to leading to more high efficiency.

2. Experimental

2.1. Synthesis of low-temperature anatase TiO2 CL

The anatase TiO2 film was prepared using a revised in situ growth method by TiF4 at 70 °C [36]. In brief, 40 mL (0.47 mmol) of HCl was added to 50 mL of deionized water to adjust the pH to 2. Then, 424 mg (0.07 M) of TiF4 was added in this solution and was stirred for 1 h. FTO substrates cleaned with acetone, ethanol, and deionized water were immersed into the above solutions and maintained at 70 °C for 0.5–6 h, in which the conductive plane was at the bottom. The samples were washed with deionized water and then dried under atmosphere at 100 °C overnight. For convenience, the CLs based on different reaction times (0.5, 1, 2, 4, and 6 h) were marked as a, b, c, d, and e, respectively, and the corresponding PVSCs were labeled as A, B, C, D, and E, respectively.

2.2. Preparation of PVSCs

PbI2 (462 mg) was dissolved in 1 mL of N,N-dimethyl formamide under stirring at 70 °C. Compact TiO2 films were covered with PbI2 by spin coating at 4500 rpm for 30 s and then dried at 100 °C for 10 min. After cooling to room temperature, the films were dipped in a solution of CH3NH3I in 2-propanol (10 mg/mL) for 30 s, rinsed with 2-propanol, and then dried at 100 °C for 30 min. The HTM was then deposited by spin coating at 4000 rpm for 30 s. This layer was composed of 72 mg/L (2,2',7',7''-tetakis(N,N-di-4-methoxyphenylamine)-9,9-spirobifluorene)(spiro-OMeTAD), 28.8 μL of 4-tert-butylpyridine, and 17.5 μL of 520 mg/mL lithium bis(trifluoromethylsulphonyl)imide in acetonitrile in 1 mL of chlorobenzene. Finally, 100 nm of Ag was evaporated on top of the device to form the metal back electrode. The active area of PVSC is 0.04 cm².

2.3. Characterization

The phase composition and crystal structure of the TiO2 films were studied via X-ray diffraction (Smart Lab, Japan). The top view and cross section of the devices were observed via field-emission scanning electron microscopy (SU8020, Japan and Merlin, Germany). The UV-vis absorption spectra were obtained using a spectrophotometer equipped with an integrating sphere setup (Lambda 950, USA). The current density–voltage curves of the PVSCs were measured using a Keithley digital source meter (Keithley 2400, USA) under a solar simulator of the AM 1.5 spectrum (100 mW cm⁻², Class AAA, Oriel, USA). The steady-state photoluminescence (PL) was measured by Fluoromax-4 (HORIBA Jovin Yvon, Edison, NJ, USA). Electrochemical impedance spectroscopy (EIS) was conducted on a computer-controlled electrochemical workstation (Zennium, Zahner, Germany) under dark conditions. The measured frequencies ranged from 100 mHz to 1 MHz, and the bias was Voc.

3. Results and discussion

Fig. 1a-e illustrate the growth process of TiO2 films along with reaction time. Clearly, the FTO substrate covered by TiO2 particles from point to surface formed the thin film and then became thicker. A change in the corresponding surface morphology was observed and shown in ESI (Fig. S1). Sample c (Fig. 1c), which was given 2 h reaction time, was expected to exhibit a high

![Fig. 1](https://example.com/figure1.png)  
**Fig. 1.** (a–e) Cross-sectional SEM images of TiO2 CLs based on different reaction times; (f) X-ray diffraction pattern for the deposited TiO2 CL on the FTO substrate.
performance because of its suitable thickness and high coverage on the FTO substrate (Fig. S1). Fig. 1f shows the XRD diffraction pattern of TiO$_2$ by in situ growth of TiF$_4$ at 70 °C. The peaks at 25.27°, 47.98°, 54.99°, and 62.0° were assigned to the (101), (200), (211), and (213) planes, respectively, which reveals that the covered thin film consisted of anatase particles (JCPDS 71-1167).

Fig. 2a illustrates a typical schematic of a planar PVSC. In this work, we constructed FTO/TiO$_2$(CL)/Perovskite/Spiro-OMeTAD (HTM)/Ag as the PVSC. The cross-sectional SEM image of the PVSC device based on sample c is shown in Fig. 2b. All functional layers could be observed and distinguished clearly. The whole device displayed good uniformity because of the in situ growth method, which is shown in ESI (Fig. S2). The surface morphology of TiO$_2$ located on the FTO substrate after 2 h is exhibited in Fig. 2c. The FTO surface is well covered by TiO$_2$ thin films with appropriate thickness and some raised nanorods (Fig. 1c). Fig. 2d shows the excellent perovskite layer formed by a two-step solution process grown on an in situ 2 h-based TiO$_2$ CL. No obvious pinhole and defect was observed. Many gaps between TiO$_2$ and perovskite existed under the other reaction times. Clear evidence is provided in ESI (Fig. S1).

The photovoltaic performances of PVSCs from A to E were measured under 1 sun illumination (AM 1.5, 100 mW cm$^{-2}$) and plotted in Fig. 3. The detailed parameters are summarized in Table 1. Obviously, the PCEs initially increased and then decreased with increasing reaction time. The unsatisfactory coverage of TiO$_2$ on the FTO substrate was observed at a short reaction time (0.5 h), which can increase the risk of contact between FTO and HTM (Fig. 1 and ESI, Fig. S1). It directly decreased the photovoltaic performance, followed by the partial short circuit of the PVSC device. The CL thickness increased with extended reaction time, which improved the coverage on the FTO substrate. Thus, the PCEs of relevant PVSCs were improved. In addition, the best perovskite layer was obtained when the TiO$_2$ reaction time was 2 h. The high coverage on TiO$_2$ was favorable for high-efficiency PVSC devices. The highest PCE was obtained by device C. The parameters of open-circuit photovoltage (V$_{oc}$), photocurrent density (J$_{sc}$), and fill factor

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Photovoltaic parameters of PVSCs based on sample A to E.</th>
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<tbody>
<tr>
<td>Samples</td>
<td>V$_{oc}$/V</td>
</tr>
<tr>
<td>A</td>
<td>0.699</td>
</tr>
<tr>
<td>B</td>
<td>0.917</td>
</tr>
<tr>
<td>C</td>
<td>0.935</td>
</tr>
<tr>
<td>D</td>
<td>0.851</td>
</tr>
<tr>
<td>E</td>
<td>0.874</td>
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were 0.935 V, 20.28 mA cm⁻², and 0.486, respectively, yielding the highest PCE of 9.22%. Thus, when the reaction time was shorter than 2 h, the lower PCE should be attributed to the partial coverage of the TiO₂ layer on FTO and the resulting partial short circuit. When the reaction time was longer than 2 h, the prolonged transport path due to the increased TiO₂ thickness should be primarily responsible for the reduced PCE.

Measurements were conducted to reveal the possible inherent mechanism underlying the differences in PCEs. Fig. 4a shows the UV–vis spectra of perovskite casting on three typical FTO/TiO₂ samples. The improved absorption for sample c due to the high coverage of perovskite for the FTO/TiO₂ surface was confirmed (ESI, Fig. S1). The steady-state photoluminescence spectra based on samples a, c, and e are shown in Fig. 4b. Sample c exhibited a faster PL decay, which suggests that the photo-induced electrons in the perovskite could be efficiently extracted by the TiO₂ layer. The above results suggest that sample c might have contributed to the high efficiency of the PVSC device. This finding is in agreement with previous IV measurements. To demonstrate further the charge transfer and recombination mechanism of the PVSC device, the EIS was used. Typically, two arcs exist in an EIS Nyquist plot. The arc at high frequency derives from the charge transport in the TiO₂ layer, HTM, and/or at HTM/Ag interface [37]. The second arc in the intermediate frequency is related to the charge recombination.

Fig. 4. (a) UV–vis spectra of perovskite casting on TiO₂ surface based on samples a, c, and e (structure: FTO/TiO₂(CH₃NH₃PbI₃), (b) Steady-state photoluminescence spectra of samples a, c, and e (structure: FTO/TiO₂(CH₃NH₃PbI₃), (c) Nyquist plots of PVSC devices based on TiO₂ samples a, c, and e under 1 sun illumination; Inset: Equivalent circuit.

Fig. 5. (a) Current-voltage characteristics of the champion cell, (b) histograms of PCE based on the sample with 27 devices, (c) and (d) J-V curves for the best PVSC measured under different scan directions and different scan rates.
resistance \( (R_{\text{rec}}) \) at the active layer. The intersection of the starting Nyquist plot and X-axis is defined as series resistance \( (R_s) \) [38–42]. Three typical PVSC devices (A, C, and E) were measured for EIS at \( V_{\text{oc}} \), bias in the dark, and the Nyquist spectra are shown in Fig. 4c. The relevant parameters were fitted according to the equivalent circuit. Three devices showed similar \( R_s \) values because of identical substrate, interface, and parallel device construction. The differences mainly existed in \( R_{\text{RTM}} \) and \( R_{\text{rec}} \). In the order of A, C, and E, the above parameters were 31.43, 35.63, and 48.46 \( \Omega \text{cm}^{-2} \) for \( R_{\text{RTM}} \) and 21.07, 176.31, and 185.62 \( \Omega \text{cm}^{-2} \) for \( R_{\text{rec}} \). Smaller \( R_{\text{RTM}} \) implies the smaller charge transfer resistance at active layers and interface. Sample E showed the largest \( R_{\text{RTM}} \), which resulted from the increasing charge transfer distance due to increased TiO\text{2} film thickness. Comparison of the \( R_{\text{rec}} \) parameters revealed that charge recombination was effectively suppressed when the reaction time exceeded 2 h. A balanced \( R_{\text{RTM}} \) and \( R_{\text{rec}} \) indicates that sample C exhibited superior performance, which is in agreement with the IV measurement results.

The current-voltage curve of the champion PVSC device is plotted in Fig. 5a. The detailed photovoltaic parameters of \( V_{\text{oc}}, R_{\text{sc}}, \) and \( FF \) were 0.922 V, 20.4 mA cm\(^{-2}\), and 0.549, respectively, yielding the highest PCE of 10.33%. Fig. 5b shows the reproduction of photovoltaic performance of 27 devices based on sample C. More than 22% of the devices showed efficiencies above 9%, and more than 44% of the devices exhibited efficiencies above 8%. The average PCE was 7.64%. We also measured the devices under different scan directions and scan rates. The corresponding J–V curves are demonstrated in Fig. 5c and d. Notably, the devices exhibited negligible hysteresis. This result indicates that low-temperature TiO\text{2} is a good alternative as a high-efficiency electron-selective layer for excellent PVSC devices.

4. Conclusion

A series of low-temperature prepared anatase TiO\text{2} thin films was successfully synthesized through the in situ growth of TiF\text{4} on the FTO substrate at 70 °C. The TiF\text{4}-derived anatase TiO\text{2} thin films were directly used as efficient Cs of all low-temperature-processed PVSCs for the first time. The PVSC with a 2 h-based TiO\text{2} CL exhibited a PCE of over 9%. The corresponding champion device achieved a high PCE of 10.33%. Investigation of the internal mechanism showed that the proper coverage and thickness of CL on FTO, the superior morphology/crystal of perovskite with no obvious pin-hole/defect, and the smallest \( R_{\text{RTM}} \) and higher \( R_{\text{rec}} \) values with excellent charge transfer and suppressed recombination in device C were responsible for the best photovoltaic performance. The low-temperature devices also exhibited good repeatability through device fabrication and measurement. This study provides an excellent preparation method for high-efficiency PVSCs at low temperature and may serve as a reference to investigate flexible PVSC devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.lectacta.2017.03.145.
Enhanced sensitized Perovskite performance

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