Fast Drying Boosted Performance Improvement of Low-Temperature Paintable Carbon-Based Perovskite Solar Cell

Qian-Qian Chu,† Bin Ding,† Yan Li,† Li–Li Gao,† Qi Qiu,‡ Cheng-Xin Li,† Chang-Jiu Li,† Guan-Jun Yang,*‡ and Baizeng Fang*§

†State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi’an Jiaotong University, 28 West Xianning Road, Xi’an, Shaanxi 710049, People’s Republic of China
‡College of Chemistry and Environmental Engineering, Shenzhen University, 3688 Nanshan Road, Shenzhen, Guangdong 518060, People’s Republic of China
§Department of Chemical & Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, British Columbia V6T 1Z3, Canada

ABSTRACT: Low-temperature paintable carbon-based perovskite solar cells have been acknowledged as a promising photovoltaic device. However, the organometal trihalide perovskite film is always degraded by the solvents in the carbon paste, resulting in a fairly low efficiency. Unfortunately, in a conventional drying process, the movements of solvent molecules from a carbon paste to atmosphere are greatly obstructed by the biscale size of carbon black and graphite, which creates an extremely long evaporation path and drying time. To solve the problem, we have developed a simple, highly efficient and scalable method, a gas pump method (GPM), to dry the carbon paste very quickly which demonstrates a 7 times drying rate compared with conventional drying. As a result, the perovskite films covered by the carbon electrode (CE) dried by the GPM keep a uniform and continuous surface morphology, and the champion solar cell reveals a conversion efficiency of 12.30% with the area of 0.1 cm² and an open circuit voltage of 1.03 V, which are much higher than those (i.e., 4.73% and 0.81 V, respectively) observed for the PSC without GPM. Furthermore, the long-time stability test shows that the solar cells with the as-prepared CE retain more than 90% of its initial power conversion efficiency after 720 h.

KEYWORDS: Low-temperature processing, Perovskite solar cell, Carbon paste, Fast drying, Gas pump method, Photovoltaic property

INTRODUCTION

The organometal trihalide perovskite acting as the light absorber in the thin film solar cells has attracted much attention due to its excellent and unique characteristics, such as appropriate direct band gap, high light-absorption efficiency, and excellent carrier transportation. 1–4 Since the first report about perovskite solar cells (PSCs) that achieved PCE of 3.8% by Miyasaka and co-workers in 2009, 5 the PSCs have experienced continuous and rapid development. Recently, the certified recorded power conversion efficiency of PSCs has increased to 22.1%. 6 The excellent PCEs also suggest that PSC is a promising candidate for conventional solar cells. 7–9 However, there still exist some barriers for commercialization of PSCs. 10–12

The commonly reported architecture of PSCs always includes a noble metal electrode, such as Au and Ag, a p-type organic small-molecular polymeric hole transporting material (HTM), such as spiro-OMeTAD and PTAA, 13,15–15 which are extremely expensive. Moreover, the related preparation methods significantly decrease the stability and hinder the industrialization of PSCs. 13,15–18 To solve this problem, the carbon-based PSCs are recently chosen as a competitive alternative because carbon materials are abundant, economical, and highly stable with a work function (~5.0 eV) to that of Au electrode (~5.1 eV). 19–21 In addition, perovskite film has previously demonstrated unique ambipolar property, acting as both the light absorber and the hole transport layer (HTL). The PSCs with carbon electrode (CE) and no HTL were first proposed by Etgar et al., and the PSCs achieved a PCE of 5%. 22 Although the manufacturing cost could be evidently reduced, the PCEs are lower compared with the PSCs with metal electrode and HTL. Therefore, many efforts have been made by researchers to tackle the problems affecting the photoelectric property of carbon-based PSCs.

Because of the instability of the organometal trihalide perovskite in most solvents, it is really difficult to prepare a
carbon layer by a solvent engineering process on the perovskite film.\textsuperscript{23–26} To avoid the dissolution of perovskite film during deposition of the carbon layer, some researchers prefabricated the carbon layer before spin coating the perovskite layer. Han et al. developed a mesoporous scaffold (TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}/NiO/carbon layer) infiltrated with the perovskite and achieved a PCE of 15%.\textsuperscript{16,17,23–29} Yang et al. achieved 11.02% efficiency by successively preparing the PbI\textsubscript{2} and CE with a subsequent treatment in a CH\textsubscript{3}NH\textsubscript{3}I bath.\textsuperscript{30–32} Meng et al. developed a freestanding thermoplastic carbon film with good conductivity and flexibility as counter electrode by hot-press on the perovskite film and obtained an efficiency of 13.53%.\textsuperscript{33} Those complex devices could be improved by directly coating a low-temperature carbon paste on the perovskite film. Consequently, some efforts have been directed toward changing the composition of CE for the simplest paintable PSCs.\textsuperscript{32–34} Some groups chose graphene carbon nanotubes as the additives, resulting in increasing production costs.\textsuperscript{35–37} Chen et al. altered the percentage of graphite and carbon black with the resultant PCEs unsatisfactory.\textsuperscript{38,39} Ma et al. changed the solvent of the carbon paste to chlorobenzene, a solvent compatible with the perovskite film, and achieved 9% efficiency based on a glass substrate and PCE of 4% based on conductive glass substrates with the sheet resistance of 15 \(\Omega\). The compact TiO\textsubscript{2} were commercially available chemicals (Weihua). The TiO\textsubscript{2} layer at 3000 rpm for 10 s. Then the sample was immediately placed under the bottom of the chamber to adjust the temperature of the sample to the drying temperature (100 °C) of the carbon paste, and the low pressure was set as 100 Pa to accelerate the drying of the carbon paste. The same operation of the device was used. When the resistance of the CE did not change with the increase of the drying time any more, the drying process was complete (Figure S1, Supporting Information).

Characterization. The surface of the perovskite films and fracture morphologies of the PSCs were characterized by a field-emission scanning electron microscope (SEM, TESCAN MIRA 3 LMH). The four-probe tests were performed on the CE of 2.5 cm \(\times\) 1.1 cm for their conductivity measurement. X-ray diffraction (XRD) patterns were acquired by a Rigaku Ultima X-ray diffractometer (Cu K\textalpha) to analyze the structure of the perovskite film. A compact steady-state spectrophotometer (Fluoromax-4, Horiba Jobin Yvon) with an excitation wavelength of 532 nm was employed to obtain the steady-state photoluminescence spectra. The photocurrent density-voltage (J–V) characteristics were measured with a Keithley 2400 source meter with an AM 1.5G filter (Sol3A, Oriel) equipped on a 450 W Class AAA solar simulator under the illumination of 100 mW/cm\textsuperscript{2}.

RESULTS AND DISCUSSION

Drying Process of Carbon Paste. Figure 1 illustrates the diagrams for the screen-printing processing of a carbon paste and the tendency for the solvent molecules to infiltrate in and dissolve the perovskite film, which is unstable in most drying processes of a carbon paste under various conditions. After a carbon paste is screen-printed on a perovskite film, the solvent molecules at the wet top surface of the carbon paste evaporate quickly and the solvent molecules are pumped away immediately, resulting in a uniform carbon electrode. Moreover, the damage of the solvent in a low-temperature commercial carbon paste to the perovskite film substantially decreases, enabling a uniform morphology of the perovskite film. As a result, the as-prepared TiO\textsubscript{2}/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/CHJ perovskite solar cells have demonstrated a PCE of 12.3%. With impressive stability, the as-developed carbon-based GPM-engineered PSCs show great potential based on the advantages such as the negligible dissolution, low electrode fabrication cost, simple and scalable low-temperature electrode preparation process, high efficiency, and excellent stability.

EXPERIMENTAL SECTION

Materials. Transparent patterned fluorine-doped tin oxide (FTO) conductive glass substrates with the sheet resistance of 15 \(\Omega\) sq\textsuperscript{−1} were scratched by laser. The carbon paste and the precursor solution of compact TiO\textsubscript{2} were commercially available chemicals (Weihua). The mesoporous TiO\textsubscript{2} (20 nm, Aldrich) paste was diluted with anhydrous ethanol (1:7 weight ratio). The lead iodide (4.61g, PbI\textsubscript{2}, 99%) and the methylmammomumium (1.59 g, CH\textsubscript{3}NH\textsubscript{3}I, PLT) were mixed and stirred in N\textsubscript{2}-N-dimethylformamide (10 mL, DMF, Sigma-Aldrich, 99.8%) at 40 °C for 8 h to prepare CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} precursor solution.

Fabrication of Perovskite Solar Cells. FTO glasses were ultrasonically cleaned by acetone, ethanol, and deionized water for 15 min respectively in succession, and then treated in the UV-zone cleaning for 30 min. Subsequently, the substrates were coated with an ~60 nm compact TiO\textsubscript{2} layer by spin-coating method at 2000 rpm for 30 s, and then sintered at 450 °C for 30 min. A 200 nm mesoporous TiO\textsubscript{2} layer was deposited on the top of the compact layer by screen-printing method and then sintered at 500 °C for 30 min. Perovskite precursor solution of 40 wt% was spin-coated on the mesoporous TiO\textsubscript{2} layer at 3000 rpm for 10 s. Then the sample was immediately transferred to the gas pump system. The system was made up of a sample chamber, a valve, a large vacuum buffer tank, and a pump. The valve was turned on, the air pressure in the sample chamber quickly decreased to the setting pressure (1500 Pa). In the vacuum environment, DMF evaporated rapidly and the evaporative molecules of the solvent were pumped away quickly. A brown, mirror-like perovskite film was formed in about 5 s. The film was annealed at 100 °C on a hot plate for 15 min. After the commercial carbon paste (main solvents, isophorone, propylene glycol monomethyl ether, and diethylene glycol monobutyl ether acetate; boiling points, 215.2, 190, and 246.8 °C, respectively) was screen-printed onto the perovskite film, the same gas pump method was used. A hot plate was placed under the bottom of the chamber to adjust the temperature of the sample to the drying temperature (100 °C) of the carbon paste, and the low pressure was set as 100 Pa to accelerate the drying of the carbon paste. When the sample was dried. As a result, the dissolution duration of the perovskite is equal to the overall duration for the drying of carbon paste. Thus, the reduction in the drying time could alleviate the damage of the solvent to the perovskite film. Figure 1c illustrates the drying process of the carbon paste with conventional method (heating in 100 °C). In the first stage, the surface of the carbon layer is wet and thus the solvents vaporize quickly. In the second stage, after the surface of the carbon paste was dried, the solvent molecules vaporize from the dry and wet interface and then get into the air environment. However, it is very difficult for the molecules to flee away from the carbon layer.\textsuperscript{35,36} At the nanoscale, there exist many twists and turns among the carbon black particles; hence the path
perovskite film on the FTO substrate can hardly influence the absorption of perovskite films. Compared with the perovskite/FTO substrate, the photoluminescence emission spectra of the perovskite/TiO2/FTO substrate display a clear quenching suggesting effective extraction of carriers by TiO2 (Figure S4b, Supporting Information). In order to obtain charge carrier lifetime, we investigated the time-resolved photoluminescence (PL) decay curves of perovskite films prepared on FTO derived from the MAPbI3 (nature drying, ND) and MAPbI3 (GPM) as shown in Figure S5. With global biexponential fits, the calculated time constants are $\tau_1 = 3.38 \pm 0.09$ ns, $\tau_2 = 52.81 \pm 0.31$ ns and $\tau_1 = 4.01 \pm 0.06$ ns, $\tau_2 = 80.13 \pm 1.09$ ns, respectively. The longer lifetime of charge carriers based on GPM indicates a lower defect concentration and a lower recombination rate.

Subsequently, the commercial carbon paste was screen-printed on the perovskite film (Figure 2b), and the sample was placed in the gas pump system. With gas pumping (Figure 2c), the solvents in the carbon paste evaporated quickly in the vacuum environment and the molecules of evaporative solvents moved rapidly away from the carbon layer to the sample chamber. In the meanwhile, the molecules of solvents in the sample chamber were pumped away immediately. Therefore, the carbon paste with GPM was dried quickly and the carbon electrode was well-prepared (Figure 2d). However, compared to the carbon paste drying without GPM, the solvents in the carbon paste evaporated slowly in the atmosphere, the gaseous molecules’ movements were disordered, and it took a long time for the molecules of solvents to escape from the carbon layer. The drying time of the carbon paste with GPM would be much shorter than that without GPM.

Because the damage degree is inversely proportional to the drying rate, the drying rates with and without GPM were investigated. Figure 3a shows that the drying rate with GPM is about 7 times as fast as the rate without GPM for the carbon pastes with different thickness, and Figure S6 (Supporting Information) shows that the drying time of the carbon pastes...
with GPM decreases about 85% relative to those without GPM. Meanwhile, the resistance of the CEs in different thickness was tested. As seen in Figure 3b, the resistances measured by the four-probe method are almost the same whether the samples with the same thickness were dried with or without GPM. According to the data for both the conductivity and the drying time, the CE prepared by GPM could decrease the dissolution time but keep as good a conductivity as the sample prepared without GPM. Based on the resistance and the drying rate, CEs with a proper thickness (about 20 μm) were utilized to prepare the PSCs. The resistance and the drying time of the CE are 24.9 Ω and 3 min, respectively.

The PSCs with CEs prepared with GPM (W/GPM) or without GPM (W/O GPM) were constructed, and SEM images were taken to observe the damage of the solvent to the perovskite film. Panels g, h, and i of Figure 4 are the morphology data of the W/GPM device. Figure 4g is the cross-sectional view of the W/GPM device; Figure 4h is the magnified image of Figure 4g; and Figure 4i is the thickness distribution of perovskite films of the W/GPM device.

Compared with the perovskite film of the device without CE (Figure 4a,b), that without GPM is destroyed seriously (Figure 4d,e), whereas that with GPM retains a dense and uniform morphology. It is evident that, with the decrease in the drying time of the carbon paste contributed by GPM, the damage to the perovskite film was substantially weakened.

In order to further compare the damage of the films W/O GPM device and W/GPM device, the localized perovskite film thickness was measured and counted. The average thicknesses of the perovskite film W/O CE device, W/GPM device, W/O GPM device are 355 ± 24 nm, 344 ± 48 nm, and 206 ± 82 nm, respectively (Figure 4c,f,i). The statistical data indicate serious destruction of the perovskite film W/O GPM device as compared with the distribution of perovskite film’s thickness W/GPM device.

Furthermore, the distribution of perovskite film’s thickness W/O GPM device is in a wider range. Interestingly, the perovskite film W/GPM device has almost the same thickness and fluctuation as the perovskite film W/O CE device, and thus

**Figure 4.** (a, d, g) Cross-sectional views of FTO/c-TiO₂/m-TiO₂/perovskite film, the film W/O GPM device, and the film W/GPM device. (b, e, h) Magnified images of panels a, d, and g, respectively. Thickness of perovskite film (c) without CE device, (f) W/O GPM device, and (i) W/GPM device.

**Figure 5.** Current–voltage characteristics (a) W/GPM device and (b) W/O GPM device. (c) Corresponding output of PCE and current density at maximum power point of 0.74 V for the champion cell under a simulated AM 1.5G solar illumination of 100 mW/cm².
it can be expected that the W/GPM device has better photoelectrical properties than the PSC without GPM.

**Photovoltaic Properties of Various Carbon-Based PSCs.** The photovoltaic performance of the two devices, prepared W/GPM or W/O GPM, were tested under an illumination of 100 mW/cm². Figure 5a shows the J–V curves of the W/GPM device, which demonstrated a PCE up to 12.3% with the area of 0.1 cm², $V_{oc}$ of 1.03 V, FF of 0.56, and $J_{sc}$ of 21.4 mA/cm². Moreover, the parameters derived in the reverse scan with a scan step of 23.7 mV and a delay time of 1000 ms are almost the same as the forward scan. Compared with the $J$–$V$ curves recorded for the W/O GPM device as shown in Figure S5b, the W/GPM device presents much higher PCE, $J_{sc}$, $V_{oc}$ and FF than the W/O GPM device. Furthermore, the output of current density and PCE at the maximum power point of the champion cell was measured at a bias voltage of 0.74 V, and as shown in Figure 5c the current density is stabilized at 15.7 mA/cm² and PCE stabilized at 11.6% in 600 s. This indicates that the W/GPM device could deliver a large PCE along with excellent output stability.

To further investigate the quality of the GPM-prepared perovskite solar cell, W/O GPM devices and 36 W/GPM devices were fabricated and the corresponding photoelectric parameters were summarized. The average PCE, $V_{oc}$, $J_{sc}$ and FF (Figure 6a–d) are $10.6 \pm 0.65\%$, $1.02 \pm 0.02$ V, $19.30 \pm 0.91$ mA/cm², and $0.54 \pm 0.03$, respectively, for the W/GPM devices. In contrast, because of the heterogeneous and discontinuous perovskite film in the W/O GPM devices which deleteriously affects charge dissociation/transport/recombination, the W/O GPM devices exhibited much worse photoelectric properties with a wide variation. The statistical parameters of the W/GPM devices and the W/O GPM devices are listed in Table S1 (Supporting Information) and Table S2 (Supporting Information). Compared with the W/O GPM devices, the excellent reproducibility of the W/GPM devices can be attributed to the higher uniformity of the CH₃NH₃PbI₃ films created by the rapid drying of the carbon paste.

To further investigate the internal electrical properties of the W/GPM device and W/O GPM device, electrochemical impedance spectroscopy (EIS) measurements were taken under white light with a power density of 100 mW/cm². Figure 7a shows the Nyquist plots from 1 MHz to 10 Hz for the W/GPM device and W/O GPM device, and are presented in Figure 7b, the W/GPM device presents much higher PCE, $J_{sc}$, $V_{oc}$ and FF than the W/O GPM device. Furthermore, the output of current density and PCE at the maximum power point of the champion cell was measured at a bias voltage of 0.74 V, and as shown in Figure 5c the current density is stabilized at 15.7 mA/cm² and PCE stabilized at 11.6% in 600 s. This indicates that the W/GPM device could deliver a large PCE along with excellent output stability.

![Figure 6.](image1)  
*Figure 6. (a) PCE, (b) open circuit voltage ($V_{oc}$), (c) short circuit current density ($J_{sc}$), and (d) fill factor (FF) of the as-constructed 36 carbon-based perovskite solar cells prepared by GPM.*

The contrast of the two curves based on the two different devices is very significant. From the enlarged image (Figure 7b), there are two circles in the frequency range for each curve. The circle at the high-frequency region (10⁶ to 10⁴ Hz) is related to the electron transfer process on the counter electrode. The second one at the intermediate frequency region (10⁴ to 10 Hz) is for the charge recombination at the TiO₂/perovskite interface. The analysis for the low frequencies (<10 Hz) would be complicated because of the multi-interfacial recombination or electron/ion diffusion. Therefore, an equivalent circuit consisting of three lumped RC circuits in series, as shown in Figure S7a, is used to fit the impedance data.

In order to clearly understand the effect of the drying process on the perovskite film, the Nyquist plots (Figure 7c,d) and Bode plots (Figure S7a,b) in different bias voltages were measured. Based on the equivalent circuit, the series resistances ($R_s$) about 12.3 Ω for W/GPM device and 23.8 Ω for W/O GPM device, suggesting high conductivity of the perovskite/carbon interface. The smaller series resistance of the W/GPM device contributes to a higher performance of PSCs, especially a higher fill factor. The charge exchange resistances ($R_{ce}$) and charge recombination resistances were derived for the W/GPM device and W/O GPM device, and are presented in Figure 7e,f, respectively. At different bias voltages, $R_{ce}$ and $R_s$ decreased with the increasing bias voltage. More importantly, $R_{ce}$ of the W/O GPM device is greater than that of the W/GPM device, indicating that the charge transfer process of the W/GPM device at the CE is more efficient. In the W/O GPM device, the perovskite film is dissolved seriously, and the dissolved...
perovskite particles nucleate and grow on the face of the carbon particles which may result in a poor contact between the carbon particles. A better charge transfer is exhibited in the W/GPM device. In Figure 7f, $R_{CE}$ of the W/O GPM device is less than that of the W/GPM device, indicating that the W/O GPM device has a poor charge extraction in the TiO$_2$/perovskite interface. The poor perovskite film morphology due to the dissolution of the perovskite particles caused by the solvents in the carbon-based PSC has been reported to be very detrimental to the device performance because this dissolution not only causes an electrical shorting but also is against the charge dissociation and transportation, and favors the charge recombination. According to the comparison of $R_{CE}$ and $R_{sh}$ between the two devices, the gas pump assisted perovskite solar cells retain good perovskite morphology, leading to excellent electrical properties.

To probe the stability of the devices, the PSCs with and without GPM were placed under ambient atmosphere and natural illumination at room temperature for 720 h. As time went on, the PCE, voltage, current density, and FF of the W/O GPM and W/GPM devices all degraded, as shown in Figure 8.

The W/O GPM devices suffered from a rapid degradation and retained less than 70% of their initial PCE after 120 h and 25% after 720 h. Interestingly, the W/GPM devices retained nearly the same PCE as its initial value after 120 h and retained more than 90% of its initial PCE after 720 h. In 720 h, the voltage, current density, and FF of the W/GPM device barely degraded. However, the values for these parameters of the W/O GPM device show a sharp decrease. Evidently, the significant difference in the long-term stability was determined by whether or not the GPM treatment was used to dry the carbon paste. The rapid drying of the W/GPM devices reduced the damage time from the solvents in the carbon paste to the perovskite film and retained the uniform morphology of the perovskite film. As a result, in the long-term stability test, the perovskite film was not easily damaged by the oxygen and water vapor in the atmosphere. In all, compared to the carbon-based PSCs prepared without GPM, these low-cost and stable PSCs fabricated with GPM are very promising photovoltaic devices.

**CONCLUSIONS**

In summary, we have successfully prepared CE through a simple and cost-effective low-temperature preparation process which could greatly increase the evaporation rate of the solvents in the carbon paste. The GPM could significantly reduce the drying time of a CE with a thickness of 20 μm from 20 to 3 min. Accordingly, the dissolution time of the perovskite film decreased considerably, and the average thickness of the perovskite film of the W/GPM device has a comparatively small decrease (i.e., from 355 to 344 nm). A PCE up to 12.3% along with a $V_{oc}$ of 1.03 V has been demonstrated by the W/GPM device. The W/GPM devices also exhibited an excellent stability, remaining nearly the same as its initial PCE after 120 h and retaining more than 90% of its initial PCE after 720 h. In all, the high reproducibility and efficiency of the devices based on GPM make it promising for the commercial production of perovskite solar cells.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01556.

XRD for the perovskite film, PL emission spectra of perovskite film on FTO and TiO$_2$/FTO, surface morphology of perovskite film, Bode plots of W/GPM and W/O GPM device, photovoltaic performance of the 36 with (or without) GPM devices, and stability test results (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

*E-mail: ygj@mail.xjtu.edu.cn (G.-J.Yang).
*Email: bfang@chbe.ubc.ca (B.F.).

ORCID

Guan-Jun Yang: 0000-0002-7753-3636
Baizeng Fang: 0000-0001-5855-7766

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The work was supported by the National Program for Support of Top-notch Young Professionals.

**REFERENCES**


