

The effect of polystyrene as binder in carbon counter electrode for mesoscopic perovskite solar cells

ZHOU Kang, CAI Chang, ZHU Yuejin *

(School of Physical Science and Technology, Ningbo University, Ningbo, 315211, China)

Abstract: The carbon electrode (CE) has the advantages in low cost, easy preparation and high efficiency, which is promising with applications in perovskite solar cells. However, owing mainly to the poor contact of carbon black and graphite, the efficiencies of the perovskite solar cell are still relatively low. In this work, we firstly use polystyrene (PS) as binder in carbon electrodes, where carbon black and graphite are well bound by PS and form a continuous conductive network. The results show that PS as binder has a significant effect on the performance of perovskite solar cells. By optimizing the quantity of PS, the power conversion efficiency (PCE) reaches 8.20% and the PCE keeps 82% of initial value after 15 days' storage.

Key words: carbon electrode; polystyrene; binder; perovskite solar cells

CLC number: O469

Document code: A

Article ID: 1001-5132 (2019) 04-0087-07

1 Introduction

Solar cells based on the organic-inorganic halide perovskite have become one of the most important research topics due to direct band gap, larger absorption coefficient and higher carrier mobility^[1-3]. Since 2009, the power conversion efficiency of PSCs has increased from 3.8%^[4] to 23%^[5]. Organic-inorganic halide perovskite has great potential application in photovoltaic industry. However, the perovskite solar cells (PSCs) use a noble metal (Au or Ag) as a counter electrode, which is not only expensive for precious metal materials, but also requires high energy deposition technology^[6-10]. At the same time, the expensive hole transport layers such as spiro-OMeTAD, poly(triarylamine) (PTAA) and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) make the increased PSC cost substantially^[11-12]. Therefore, there is an important

practical value in the search for inexpensive, stable materials to replace noble metals as counter electrodes. Carbon materials have not only the characteristics of structural diversity, chemical stability and rich surface chemical properties, but also the advantages of low price and easy preparation^[13-18]. At the same time, the work function of carbon is similar to that of Au. It is a better choice to replace the noble metal electrode by carbon materials.

In 2013, Hu et al^[19] firstly prepared the carbon counter electrode in PSC without hole transport material (HTM). Since then, carbon electrodes instead of Pt and Au electrodes have been applied as cathode for solar cells. The conductive mechanism of carbon electrode is complex. Furthermore, excellent electrode conductivity requires intimate contact and cross linked conductive network formed between carbon materials in carbon electrodes. The quality of carbon electrode is

收稿日期: 2019-02-26. 宁波大学学报(理工版) 网址: <http://journal.lg.nbu.edu.cn/>

基金项目: 国家自然科学基金(11374168); 宁波大学王宽诚幸福基金.

第一作者: 周康(1993-), 男, 商丘河南人, 在读硕士研究生, 主要研究方向: 钙钛矿太阳能电池. E-mail: 15058453762@163.com

*通信作者: 诸跃进(1958-), 男, 浙江临安人, 教授, 主要研究方向: 新能源材料. E-mail: zhuyuejin@nbu.edu.cn

determined by the composition of carbon paste. Carbon paste is a thick paste, which is made of carbon materials, binder and solvent. The main function of the binder is to connect carbon materials together. Wei et al^[7] used polyvinyl acetate as a binder, successfully prepared a good carbon electrode and obtained a perovskite solar cell with an efficiency of 13.53%. Commercial carbon paste composed of carbon black, graphite and epoxy as binder achieves an efficiency of 11.49% of the carbon electrode PSC^[20]. Kay et al^[21] used a carbon electrode with a particle size of about 20 nm TiO₂ nanocrystals as binder instead of a noble metal electrode to obtain a dye-sensitized solar cell with a conversion efficiency of 6.67%. Zhang et al^[8] used ZrO₂ nanoparticles as binder to obtain a carbon electrode PSC with an efficiency of 12.84%. Besides, using ethyl cellulose as binder, low-temperature and highly stable mesoscopic PSC with an efficiency of 7.29% was obtained in our previous work^[22]. Exploring conductive carbon film from materials (solvent, binder, conductive carbon black and graphite) under low temperature and their compatibility with perovskite are very critical. Solvents must be environment-friendly and contain negligible combustible materials, and the binder itself needs to be compatible with the solvent.

Here, we successfully achieved highly-conductive carbon electrode by using PS as binder to promote inter-particle contact in a carbon paste. By optimizing the quantity of PS, the PCE reached 8.20% and the average PCE was 7.9%. The results show that PS as binder has a significant effect on the device performance. This carbon electrode has the advantages of low cost and easy preparation, thus has broad application prospects in PSCs.

2 Experiment

2.1 Fabrication of carbon paste

The carbon pastes were composed of carbon material (1.5 g graphite powder and 0.5 g carbon black), 12 mL ethyl acetate and PS (0.4 g, 0.6 g and 0.8 g). A

series of carbon paste was prepared by changing the mass fraction of PS (20 wt%, 30 wt% and 40 wt%, the samples are referred to A, B and C, respectively) in the mixture of carbon materials. Then all the three mixtures were followed by ball milling for 3 h.

2.2 Fabrication of mesoscopic perovskite solar cell

First, fluorine-doped tin oxide (FTO) coated glass substrates were etched by hydrochloric acid before ultrasonically cleaned with ultrasonication in aqueous washing solution, ethanol and acetone for 15 min. Afterwards, the substrates were further treated with ultraviolet ozone treatment for 15 min. After that, the patterned substrates were coated with an 80 nm compact TiO₂ layer by spin-coating at 4 000 r·min⁻¹ for 30 s, and annealed at 450 °C for 30 min. Then, for a mesoporous TiO₂ layer (120 nm), a diluted TiO₂ paste (Dyesol 18 NR-T, 1:4 attenuation by weight in ethanol) was spin-coated at 5 000 r·min⁻¹ for 30 s, which was dried at 120 °C for 15 min, and annealed at 500 °C for 30 min in air condition. After cooling to room temperature, 30 min in TiCl₄ water solution at 70 °C and rinsing with deionized water. Drying at 120 °C for 15 min and then annealing at 500 °C for 30 min.

The concentration of the mixed solution of the perovskite (CH₃NH₃PbI₃) precursor solution was 1.3 mol·L⁻¹ which was synthesized by mixing CH₃NH₃I₃ (0.206 7 g) and PbI₂ (0.599 3 g) into 0.7 mL DMF and 0.3 mL DMSO was stirred at 70 °C, until the mixed solution was luminously yellow. The precursor solution was spin-coated on TiO₂ substrates at 1 000 r·min⁻¹ for 5 s and 5 000 r·min⁻¹ for 25 s in a N₂-filled glovebox. During the spinning process, 0.4 mL chlorobenzene as anti-solvent was dripped to rush the film. After being annealed at 100 °C for 10 min, a brilliant black film of perovskite film (600 nm) was obtained. Then, a carbon paste directly deposited on perovskite film by a doctor-blading method to form carbon electrodes (20 μm).

2.3 Characterizations

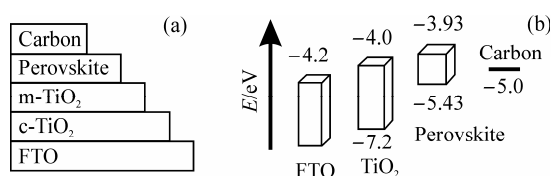
The morphology of the samples was characterized by scanning electron microscopy (SEM; SU-8010, Japan). The current density-voltage measurements were

conducted under simulated AM1.5G sunlight of $100 \text{ mW} \cdot \text{cm}^{-2}$ using an AM1.5G type filter (Newport, 81904, USA). The light intensity was adjusted by a standard Si solar cell. Electrochemical impedance spectroscopy (EIS) measurements were carried out under dark bias at 0.85 V bias, with an amplitude of 10 mV and a frequency range of 100 MHz to 100 mHz. The incident photo-current conversion efficiency (IPCE) spectra were measured in air under the irradiation of a 300 W Xenon light source with an oriel corner stone monochromator in DC mode. Before the sample is measured, the Si detector is used for reference scanning to reduce background.

3 Results and discussion

3.1 Structure of HTM-free $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ mesoscopic solar cells

Fig. 1(a) shows the device structure of HTM-free $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{C}$ mesoscopic perovskite solar cells. Fig. 1(b) shows the energy levels of TiO_2 , $\text{CH}_3\text{NH}_3\text{PbI}_3$ and carbon. Once illuminated by sunlight, free electrons and holes are generated in $\text{CH}_3\text{NH}_3\text{PbI}_3$. Afterwards, electrons pass through the electron transport layer to the FTO layer, and holes are injected into the carbon electrode.



(a) The schematic structure of mesoscopic perovskite solar cells based on carbon counter electrode; (b) The energy band diagram of the materials used in the device.

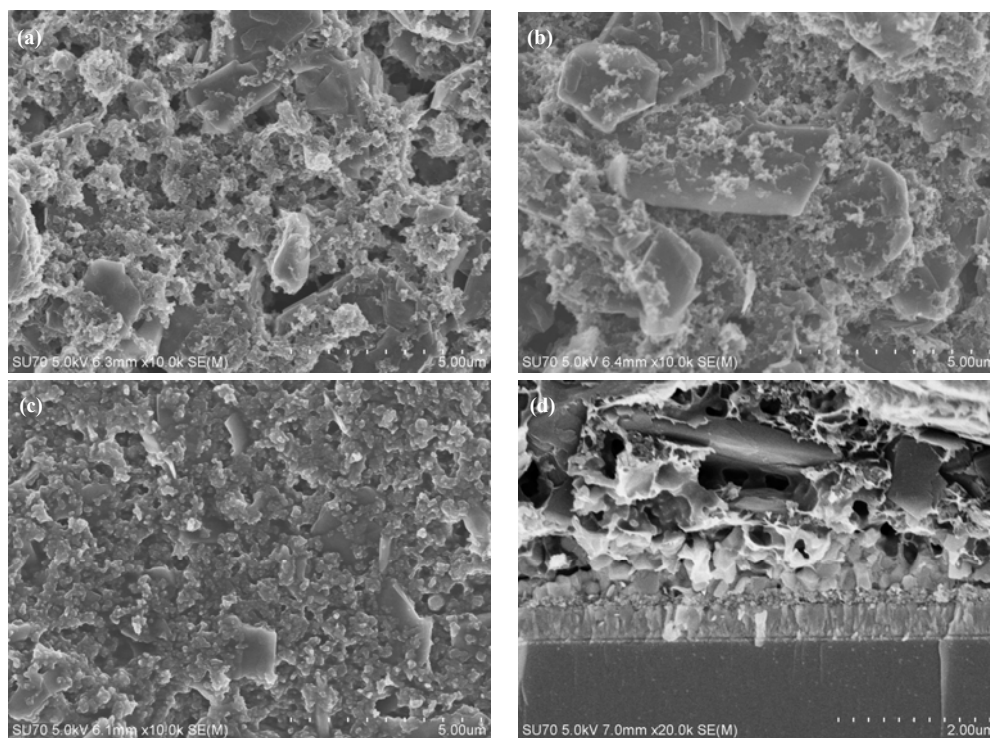
Fig. 1 The Structure of mesoscopic perovskite solar cells and the energy band

3.2 Characterization of devices with different contents of PS in carbon electrodes

We first examine the surface image of carbon electrodes by scanning electron microscopy (SEM). Fig. 2(a) shows the surface morphology of CE A, which is composed of 20 wt% PS. Intimate contact between

carbon materials is crucial to obtaining high conductivity, which is greatly influenced by the properties of the binder. PS is used as binder in carbon paste to bind carbon black with graphite. Carbon black nanoparticles fill the gaps among the graphite flakes, and there exist some pores on the carbon surface at 20% PS content, which will not be beneficial for electrons transport and might decrease the photovoltaic performance. Fig. 2(b) shows the surface morphology of CE B. We can clearly see graphite flakes and carbon black particles on the surface. PS of 30% content can better bind the carbon black and graphite, so carbon black fills interparticle voids over from the graphite flakes facilitating electrical interconnection, which might improve the efficiency of solar cells. Fig. 2(c) shows the surface morphology of CE C, which is composed of 40 wt% PS. A large number of PS covers graphite and carbon black on the surface. The insulating PS might result in poor conductivity of carbon electrodes, leading to reduction of the efficiency of PSCs. Fig. 2(d) shows the cross-sectional SEM image of CE B which depicts a uniform deposition. As a key influence, the contact between carbon black and graphite is an important factor for improving the performance of carbon electrode based PSC.

The photocurrent density-voltage curves of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CE}$ devices with different contents of PS in CEs are displayed in Fig. 3. The photovoltaic performances of devices with different CEs are characterized by current density—voltage (J — V) measurements under simulated AM1.5G solar irradiation at $100 \text{ mW} \cdot \text{cm}^{-2}$ in air (Fig. 3), and the corresponding data are summarized in Table 1. The optimized device based on CE A shows a poor short-circuit current density (J_{sc}) of $13.10 \text{ mA} \cdot \text{cm}^{-2}$, an open-circuit voltage (V_{oc}) of 0.87 V, and a fill factor (FF) of 0.544 leading to a PCE of 6.2%. The photovoltaic performances of devices are improved with the increase of PS contents in CEs. When PS is 30% of the carbon material, V_{oc} , J_{sc} , FF and PCE of the device are increased to 0.94 V, $15.77 \text{ mA} \cdot \text{cm}^{-2}$, 0.569 and 8.2% respectively. However, when the contents of



(a), (b) and (c) show the surface image of different contents of PS in CEs of CE A, B, and C respectively, (d) shows the cross-sectional image of CE B.

Fig. 2 Top view SEM images of different samples

PS are further increased, the efficiencies of devices are decreased. The device shows a V_{oc} of 0.90 V, a J_{sc} of $14.25 \text{ mA} \cdot \text{cm}^{-2}$, an FF of 0.568, resulting in a poor efficiency of 7.3%. The improvement of device efficiency can be attributed to the binding of carbon black and graphite with PS, thus improving the performance of PSCs. The poor performance for the device with more content of PS in CEs could be due to the poor conductivity of PS, which leads to low PCE value for the device.

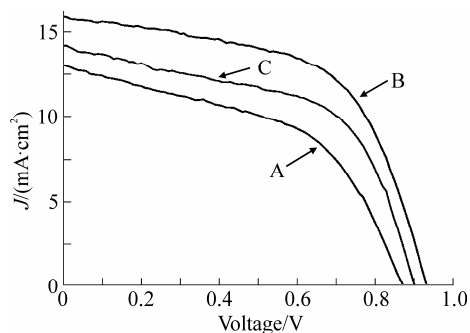


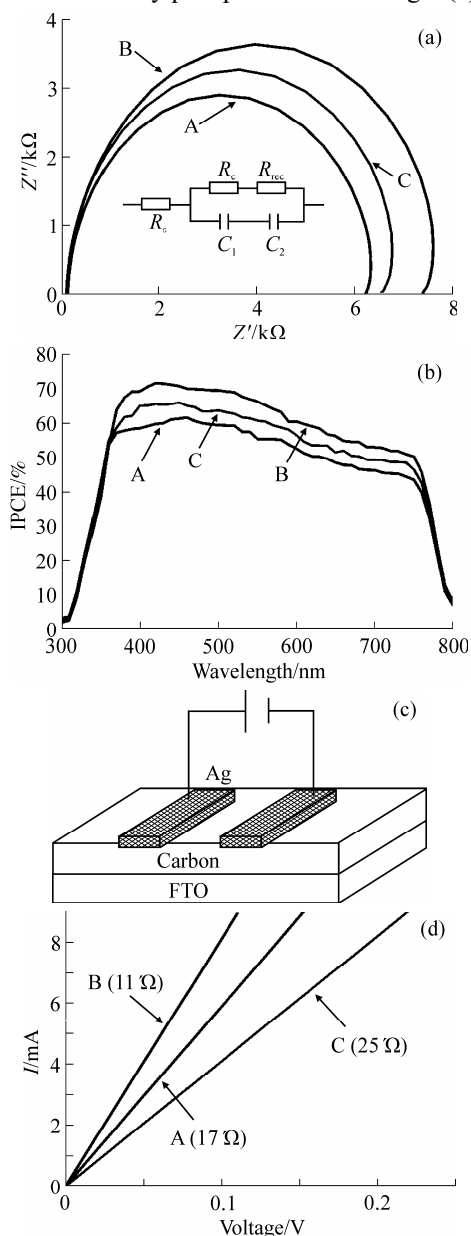
Fig. 3 Current density—voltage (J — V) curves of different PSCs (A, B, C)

Table 1 Photovoltaic properties of HTM-free $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ mesoscopic perovskite solar cells with different PSCs (PCE, J_{sc} , V_{oc} , FF extracted from the data in Fig. 3)

CE sample	V_{oc}/V	$J_{sc}/(\text{mA} \cdot \text{cm}^{-2})$	FF	PCE/%
A	0.87	13.10	0.544	6.2
B	0.94	15.77	0.569	8.2
C	0.90	14.25	0.568	7.3

The electrochemical impedance spectroscopy (EIS) of the different CEs are measured under dark condition at different forward applied bias to investigate the internal charge transport properties. The Nyquist plots of cells with CE A, B, C are presented in Fig. 4(a). The Nyquist plots of the devices are measured at -0.80 V in the frequency ranging from 1 MHz to 100 mHz in dark. The equivalent circuit can be simplified to the circuit model shown in the inset of Fig 4(a). The series resistance (R_s) is deduced in the region near $Z'=0$. In this paper, we focus on the discussion of series resistance (R_s) and charge transfer resistance between CEs and perovskite in consideration of relevance to the CEs.

According to the results, R_s is changed under different CEs for all these three kinds of devices, as shown in Fig. 4(b). The result implies that the better contact between carbon black/graphite and carbon particles/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ will be beneficial for hole transport. The series resistance of the carbon counter electrode are showed in Table 2. From the Nyquist plots shown in Fig. 4(a), R_s of



(a) Nyquist plots for PSCs prepared with CEs of different CE A, B, C; (b) IPCE cures for devices based on CE A, B, C; (c) The schematic structure of carbon/Ag; (d) Resistance of different carbon electrodes.

Fig. 4 EIS of the different CEs

136, 119 and $144\ \Omega$ are obtained with deffierent CEs. The series resistance R_s of PSC based on CE B is $119\ \Omega$. However, when PS is 40% of the carbon material, it shows a relatively large R_s value. PS as binder applied in CEs has a certain effect on R_s . This can be attributed to poor conductivity of PS and PS filled with most carbon materials resulting in high series resistance. Accordingly, the devices based CE B have a better performance due to their lower value of total series resistance.

Table 2 Series resistance of the different CEs Ω

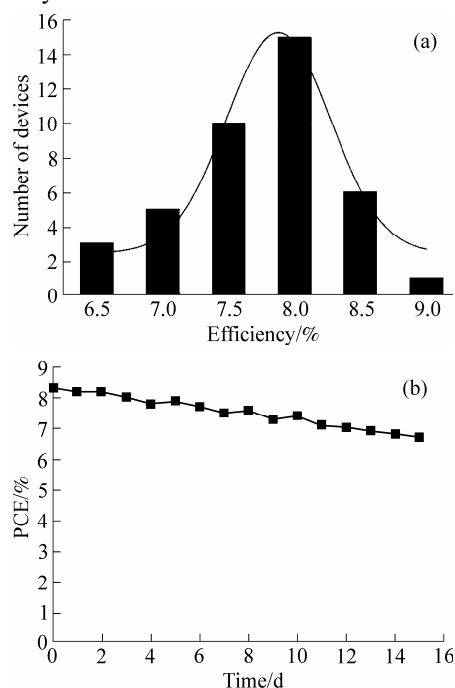
Item	A	B	C
R_s	136	119	144

To grasp deeper insight into the binder roles played by CEs, we measured the incident IPCE curves of the devices with different PS. As shown in Figure 4(b), it is quite evident that IPCE curves for devices based on CEs A, B, C. Obviously, due to more effective charge collection/extraction, CE B gives noticeable improvement of the photo current density in the whole visible region from 400 to 800 nm. PS binds the carbon black and graphite together, reducing the charge recombination. The effective charge extraction decreases the carrier density within the CEs, which eventually brings down the rate of recombination.

The resistance measurement of carbon electrode is based on measuring I — V curve by Ag plating on carbon electrode in Fig. 4(c). Fig. 4(d) contains specific I — V curves of different carbon electrodes (sheet resistance (slope) = voltage / current). The resistance of different carbon electrodes is 17, 11, $25\ \Omega$, respectively. When PS is 30% of the carbon material, the resistance of carbon electrodes is the smallest, which may contribute to the transport of charges. From the above analysis, we can conclude that 30% PS improves the charge transport of carbon counter electrode and reduces the interface recombination, which results in better device performance.

In order to confirm the repeatability of the results, 40 separate devices were prepared using the optimized experimental conditions. The direct illustration of the

PCE is shown in Fig. 5(a). The results show that their average PCE is 7.9%, indicating that it has good reproducibility. To further confirm the long-term stability of the PSCs in ambient air, PCE measurement of the CE B is characterized periodically in the dark. Fig. 5(b) shows the efficiency of the device during 15 days after been fabricated. The PCE changes from initial 8.2% to 6.7% with a 18% drop after 15 days. Device with CE B retained 82% of its initial efficiency after 15 days. Obviously, the solar cells with carbon CE B can exhibit good stability. This stability may be attributed to the thick carbon film (20 μm) covered on $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, which can also work as a protecting layer against the humidity and protect the $\text{CH}_3\text{NH}_3\text{PbI}_3$ from invasion of humidity.



(a) The histograms of device CE B efficiency measured for 40 separate perovskite solar cells; (b) The stability test of the champion cell stored in ambient atmosphere at room temperature measured under one sun illumination.

Fig. 5 The illustration of the PCE and efficiency of device

4 Conclusions

The contact between carbon black and graphite is an important factor affecting the performance of carbon

electrode perovskite solar cells. In a word, PS in the carbon paste is firstly used as binder to bind carbon black and graphite, which improves the performance of carbon based PSCs. By optimizing the quantity of PS, we have effectively improved the contact between carbon particles and carbon/perovskite interface. When PS is 30% of the weight of the carbon material, the best performance can be obtained. This work shows PS as binder improves both the performance and the stability of perovskite solar cells.

References:

- [1] Mosconi E, Amat A, Nazeeruddin M K, et al. First principles modeling of mixed halide organometal perovskites for photovoltaic applications[J]. The Journal of Physical Chemistry C, 2013, 117(27):13902-13913.
- [2] Eperon G E, Stranks S D, Menelaou C, et al. Formamidinium lead trihalide: A broadly tunable perovskite for efficient planar heterojunction solar cells[J]. Energy & Environmental Science, 2014, 7(3):982-988.
- [3] Kojima A, Ikegami M, Teshima K, et al. Highly luminescent lead bromide perovskite nanoparticles synthesized with porous alumina media[J]. Chemistry Letters, 2012, 41(4):397-399.
- [4] Kojima A, Teshima K, Shirai Y, et al. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells[J]. Journal of the American Chemical Society, 2009, 131:6050-6051.
- [5] Zhao D W, Wang C H, Song Z M, et al. 4-terminal all-perovskite tandem solar cells achieving power conversion efficiencies exceeding 23%[EB/OL]. [2018-10-11]. https://pubs.acs.org/ccindex.cn/doi/suppl/10.1021/acsenerylett.7b01287/suppl_file/nz7b01287_si_001.pdf.
- [6] Xiao M D, Huang F Z, Huang W C, et al. A fast deposition crystallization procedure for highly efficient lead iodide perovskite thin-film solar cells[J]. Angewandte Chemie, 2015, 53:9898-9903.
- [7] Wei H Y, Xiao J Y, Yang Y Y, et al. Free-standing flexible carbon electrode for highly efficient hole-conductor-free perovskite solar cells[J]. Carbon, 2015, 93:861-868.
- [8] Zhang L J, Liu T F, Liu L F, et al. The effect of carbon counter electrode on fully printable mesoscopic perovskite solar cell[J]. Journal of Materials Chemistry A, 2015(3):9165-9170.
- [9] Mei A, Li X, Ku Z, et al. A hole-conductor-free, fully

- printable mesoscopic perovskite solar cell with high stability[J]. *Science*, 2014, 345(6194):295-298.
- [10] Liu L, Mei A, Liu T, et al. Fully printable mesoscopic perovskite solar cells with organic silane self-assembled monolayer[J]. *Journal of the American Chemical Society*, 2015, 137:1790-1793.
- [11] Zhang F, Yang X, Wang W, et al. Boosting the efficiency and the stability of low cost perovskite solar cells by using CuPc Nanorods as hole transport material and carbon as counter electrode[J]. *Nano Energy*, 2016, 20: 108-116.
- [12] Zhang F, Song J, Hu R, et al. Interfacial passivation of the p-doped hole-transporting layer using general insulating polymers for high-performance inverted perovskite solar cells[J]. *Small*, 2018, 14(19):e1704007.
- [13] Yang Y Y, Xiao J Y, Wei H Y, et al. An all-carbon counter electrode for highly efficient hole-conductor-free organo-metal perovskite solar cells[J]. *RSC Advances*, 2014, 95:52825-52830.
- [14] Murakami T, Grätzel M. Counter electrodes for DSC: Application of functional materials as catalysts[J]. *Inorganica Chimica Acta*, 2008, 361(3):572-580.
- [15] Liao G L, Liu Z Y, Sun B, et al. Enhanced photovoltaic performance and stability of carbon counter electrode based perovskite solar cells encapsulated by PDMS[J]. *Journal of Materials Chemistry A*, 2016, 27(4):10700-10709.
- [16] Zhang F G, Yang X C, Cheng M, et al. Engineering of hole-selective contact for low temperature-processed carbon counter electrode-based perovskite solar cells[J]. *Journal of Materials Chemistry A*, 2015, 48(3):24272-24280.
- [17] Gholipour S, Domanski K, Matsui T, et al. Highly efficient and stable perovskite solar cells based on a low-cost carbon cloth[J]. *Advanced Energy Materials*, 2016, 6: 1601116-1601122.
- [18] Wang H, Hu X, Chen H. The effect of carbon black in carbon counter electrode for $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ heterojunction solar cells[J]. *RSC Advances*, 2015, 5(38): 30192-30196.
- [19] Ku Z L, Rong Y G, Xu M, et al. Full printable processed mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ heterojunction solar cells with carbon counter electrode[J]. *Scientific Reports*, 2013 (3):3132-3135.
- [20] Zhang Y, Zhou K, Zhang J, et al. Vibration treated carbon electrode for highly efficient hole-conductor-free perovskite solar cells[J]. *Organic Electronics*, 2018, 52: 159-164.
- [21] Kay A, Grätzel M. Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder[J]. *Solar Energy Materials & Solar Cells*, 1996, 44:99-117.
- [22] Yue G, Chen D, Wang P, et al. Low-temperature prepared carbon electrodes for hole-conductor-free mesoscopic perovskite solar cells[J]. *Electrochimica Acta*, 2016, 218: 84-90.

聚苯乙烯作为粘结剂的碳基钙钛矿太阳能电池的研究

周 康, 蔡 畅, 诸跃进*

(宁波大学 物理科学与技术学院, 浙江 宁波 315211)

摘要: 碳电极具有成本低、制备方便、效率高等优点, 在钙钛矿太阳能电池中具有广阔的应用前景. 首次使用聚苯乙烯作为制备碳电极的粘结剂, 实验结果表明, 聚苯乙烯作为粘结剂对钙钛矿太阳能电池的性能有显著影响. 通过优化聚苯乙烯浓度的量, 碳基钙钛矿太阳能电池光电转换效率达到了 8.20%, 在存储 15 d 后, 光电转换效率仍保持初始值的 82%.

关键词: 碳电极; 聚苯乙烯; 粘结剂; 钙钛矿太阳能电池

(责任编辑 章践立)