Improving the performance of perovskite solar cells with glycerol-doped PEDOT:PSS buffer layer*

Jian-Feng Li(李建丰)†, Chuang Zhao(赵创), Heng Zhang(张恒), Jun-Feng Tong(同军锋), Peng Zhang(张鹏), Chun-Yan Yang(杨春燕), Yang-Jun Xia(夏养君)‡, and Duo-Wang Fan(范多旺)

Key Laboratory of Optoelectronic Technology and Intelligent Control of Ministry Education, Lanzhou Jiaotong University, Lanzhou 730070, *China*

(Received 25 June 2015; revised manuscript received 22 October 2015; published online 20 December 2015)

In this paper, we investigate the effects of glycerol doping on transmittance, conductivity and surface morphology of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (PEDOT:PSS) and its influence on the performance of perovskite solar cells. . The conductivity of PEDOT:PSS is improved obviously by doping glycerol. The maximum of the conductivity is 0.89 S/cm when the doping concentration reaches 6 wt%, which increases about 127 times compared with undoped. The perovskite solar cells are fabricated with a configuration of indium tin oxide (ITO)/PEDOT:PSS/$CH_3NH_3PbI_3$/$PC_{61}BM$/Al, where PEDOT:PSS and $PC_{61}BM$ are used as hole and electron transport layers, respectively. The results show an improvement of hole charge transport as well as an increase of short-circuit current density and a reduction of series resistance, owing to the higher conductivity of the doped PEDOT:PSS. Consequently, it improves the whole performance of perovskite solar cell. The power conversion efficiency (PCE) of the device is improved from 8.57% to 11.03% under AM 1.5 G (100 mW/cm^2 illumination) after the buffer layer has been modified.

Keywords: glycerol, PEDOT:PSS, perovskite solar cells

PACS: 84.60.Jt, 88.40.H–, 84.60.Bk **DOI:** 10.1088/1674-1056/25/2/028402

1. Introduction

Perovskite solar cells based on organometal halide light absorbers have been considered as a promising photovoltaic technology due to their direct bandgap, high absorption coefficient, long exciton diffusion length, and excellent charge transport properties that lead to their superb power conversion efficiency (PCE).[1–6] Typical perovskite solar cells have employed an electron-transport layer (ETL)/perovskite material/hole-transport layer (HTL) structure. Initial meso-superstructured-type solar cells based on a mesoporous TiO_2 layer as the electron-transport layer require high-temperature processing ($> 450\ ^\circ$C), which hinders the commercialization.[7–9] Therefore, many approaches have been developed to avoid the high-temperature barrier. One promising approach, a planar heterojunction device architecture, is particularly interesting, owing to its simple cell configuration and possible low-temperature fabrication.[10–12] Sun *et al.*[10] first reported the planar heterojunction perovskite solar cells, in which PEDOT:PSS was used as the hole transporter and fullerene derivatives as the electron transporter. However, the electrical conductivity of PEDOT:PSS thin film is generally low, the introduction of a PEDOT:PSS buffer layer in the solar cell inevitably increases the series resistance of the whole device, affecting the short circuit current density (J_{SC}) and the fill factor (FF). Many promising techniques have been developed to mainly improve the electrical property of PEDOT:PSS, mostly by exposing PEDOT:PSS to selective reagents in polymer solar cells. For example, the addition of various organic solvents, surfactants, salts, and acids such as H_2SO_4,[13] dimethyl sulfoxide (DMSO),[14] methanol,[15] Zonyl FS-300,[16] N,N-dimethyl for mamide (DMF),[17] tetrahydrofuran (THF), acetonitrile (ACN), isopropyl alcohol (IPA)[18] and sorbitol[19] led to significantly enhanced electrical properties of PEDOT:PSS films. Meanwhile, it was reported that many properties of PEDOT:PSS such as transmittance, morphology, and work function would be changed when the low conductivity PEDOT:PSS was doped with different polar solvents or organic compounds in polymer solar cells. To the best of our knowledge, there is little in the literature reporting on the effect of the addition of some solvent additives to the PEDOT:PSS on the performance of perovskite solar cells.

Therefore, we analyze the changes of transparency, electrical conductivity and surface morphology of PEDOT:PSS thin film doped with glycerol of different concentrations, as well as the influence of doped PEDOT:PSS thin film on the performance of a perovskite solar cell. The results indicate that the perovskite solar cell

*Project supported by the National Natural Science Foundation of China (Grant Nos. 61264002, 61166002, 91333206, and 51463011), the Natural Science Foundation of Gansu Province, China (Grant No. 1308RJZA159), the New Century Excellent Talents in University of Ministry of Education of China (Grant No. NCET-13-0840), the Research Project of Graduate Teacher of Gansu Province, China (Grant No. 2014A-0042), and the Postdoctoral Science Foundation from Lanzhou Jiaotong University, China.

†Corresponding author. E-mail: ljfpyc@163.com

‡Corresponding author. E-mail: yjxia73@126.com

© 2016 Chinese Physical Society and IOP Publishing Ltd

with ITO/PEDOT:PSS/$CH_3NH_3PbI_3$/$PC_{61}BM$/Al configuration, which is prepared by doping 6% glycerol into the PEDOT:PSS, achieves an open-circuit voltage (V_{OC}) of 0.85 V, a J_{SC} of 17.92 mA·cm^{-2}, fill factor (FF) of 72.39%, and power conversion efficiency (PCE) of 11.03%, where the cell's efficiency increases 28.70% compared with un-doped ones. Hence, doping glycerol into PEDOT:PSS is an important method to improve the efficiency of a perovskite solar cell.

2. Experiment

As shown in Fig. 1, the perovskite solar cells (PSCs) were fabricated with a configuration of indium tin oxide (ITO)/PEDOT:PSS/$CH_3NH_3PbI_3$/$PC_{61}BM$/Al. Patterned indium tin oxide(ITO)-coated glass with a sheet resistance of 15 Ω/square–20 Ω/square was cleaned by a surfactant scrub, then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water, followed by acetone and isopropanol. After oxygen plasma cleaning for 14 min, a 40-nm thick poly(3,4-ethylene- dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto an ITO substrate and then dried at 160 °C for 30 min. PbI_2 and CH_3NH_3I were dissolved in N,N-dimethylformamide (DMF) and 2-propanol with concentrations of 400 mg·ml^{-1} and 30 mg·ml^{-1}, respectively. The PbI_2 solution was heated at 80 °C for around 20 min before use to make sure that PbI_2 can be fully dissolved. The hot PbI_2 solution was spun on the PEDOT:PSS substrates at 2000 rpm for 30 s. Then they were transferred onto a hot plate quickly and dried at 100 °C for 3 min. The CH_3NH_3I solution was spun on the tops of dried PbI_2 films at 2000 rpm for 30 s at room temperature. The spin coated PbI_2/CH_3NH_3I stacking films were then placed on the top of a hot plate that has been preheated at 100 °C in the ambient conditions. Around 25 μL of DMF solvent was added at the edge of a petri dish and quickly covered the perovskite layers to form the DMF vapor atmosphere. This annealing process continued for 1 h, leading to the formation of $CH_3NH_3PbI_3$ layers of about 250 nm. Subsequently, the $PC_{61}BM$ solution was spin-coated over a perovskite layer at 1000 rpm for 40 s. Finally, a 100-nm Al layer was evaporated with a shadow mask in sequence in a vacuum chamber at a pressure of 6×10^{-5} Pa. The overlapping area between the cathode and anode determines a pixel size of 0.1 cm^2. The thickness values of the evaporated Al were monitored by a quartz crystal thickness/ratio monitor ((SI-TM206, Shenyang Sciens Co.). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere in a nitrogen drybox (Etelux Co.) containing less than 1-ppm oxygen and moisture. The power conversion efficiencies (PCEs) of the resulting perovskite solar cells were measured under 1 sun, AM 1.5G (Air mass 1.5 global) condition using a solar simulator (XES-70S1, San-EI Electric Co.) with an irradiation of 100 mW·cm^{-2}. The current density–voltage (J–V) characteristics were recorded with a Keithley 2400 source-measurement unit. The spectral responses of the devices were measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Bejing 7-star Opt. In. Co.). A calibrated silicon detector was used to determine the absolute photosensitivity.

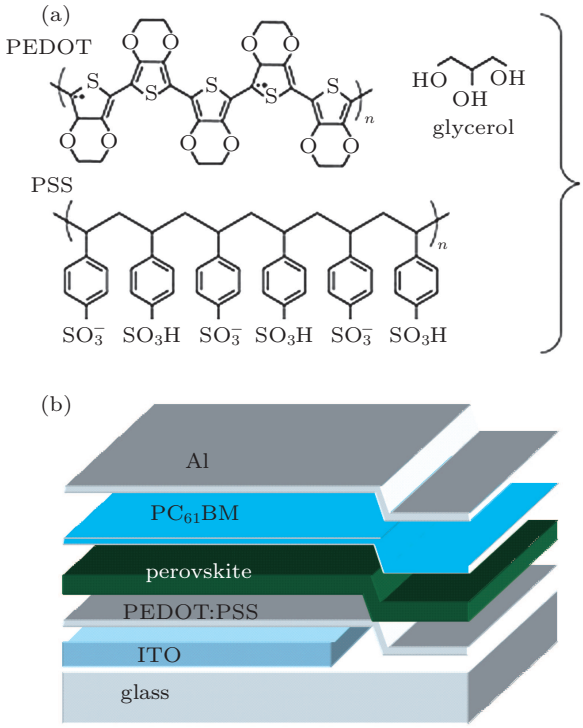


Fig. 1. (color online) (a) Chemical structure of PEDOT:PSS, glycerol and (b) the structure of the perovskite solar cells.

3. Results and discussion

3.1. Effect of glycerol doping on transmittance of PEDOT:PSS film

To better understand that the transparency of doped PEDOT:PSS thin film will influence the numbers of incident photons and photon-generated carriers on the perovskite layer, we test and compare the transparency values of the PEDOT:PSS thin films before and after doping four different glycerol concentrations; the results are shown in Fig. 2. It can be seen that the transparency of glycerol-doped PEDOT:PSS thin film declines slightly in the waveband between 370 nm and 450 nm; the transparency of glycerol-doped PEDOT:PSS thin film improves slightly in the waveband between 450 nm and 600 nm; the transparency of PEDOT: PSS thin film remains largely unchanged in the waveband between 600 nm and 800 nm. Since the average transparency of the whole thin film shows little change, there is no direct relationship between the performance improvement of a glycerol-doped PEDOT:PSS perovskite solar cell and the thin film transparency.

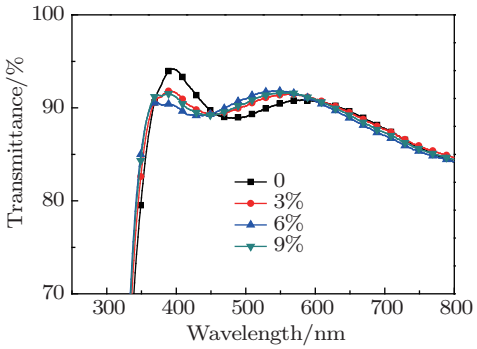


Fig. 2. (color online) Effects of glycerol content on transmittance of PEDOT:PSS films.

3.2. Effect of glycerol doping on conductivity of PEDOT:PSS film

Figure 3 shows the conductivities of glycerol-treated PEDOT:PSS films for various doping concentrations, which are measured by using the four-point probe technique; data for a pristine PEDOT:PSS film under the same conditions are also shown for comparison. Figure 3 follows that the electrical conductivity of the PEDOT:PSS thin film first increases, then decreases, with increasing glycerol content. The electrical conductivity of the PEDOT:PSS thin film without glycerol doping is 0.007 S/cm; the electrical conductivity of the PEDOT:PSS thin film with 3% glycerol doping reaches 0.684 S/cm; the electrical conductivity of the PEDOT:PSS thin film with 6% glycerol doping reaches 0.891 S/cm; however, further glycerol increase will result in a slight reduction of the electrical conductivity of the PEDOT:PSS thin film. Kim *et al.*[20] proposed that the conductivity enhancement is due to the fact that polar organic solvents with higher dielectric constant induce a screening effect between counter ions and charge carriers, which reduces the electrostatic interaction between positively charged PEDOT and negatively charged PSS, thereby enhancing the hopping rate in the PEDOT:PSS film. Meanwhile, Shin *et al.*[21] believed that the increased conductivities of the films in the presence of organic solvents arise from the rearrangement of the PEDOT:PSS morphology and PEDOT particle agglomerations occur, which leads to better connections between the conducting PEDOT chains.

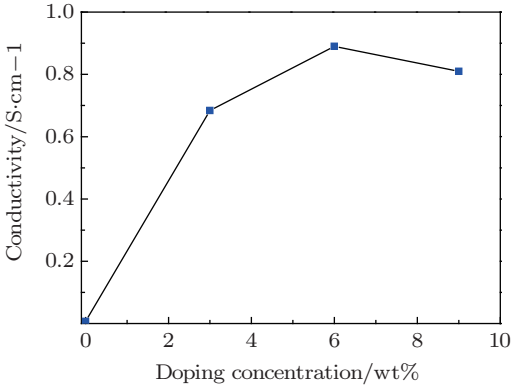


Fig. 3. (color online) Effect of glycerol content on conductivity of PEDOT:PSS film.

3.3. Effect of glycerol doping on surface morphology of PEDOT:PSS film

Atomic force microscopy (AFM) is used to characterize the surface morphology of the PEDOT:PSS film as shown

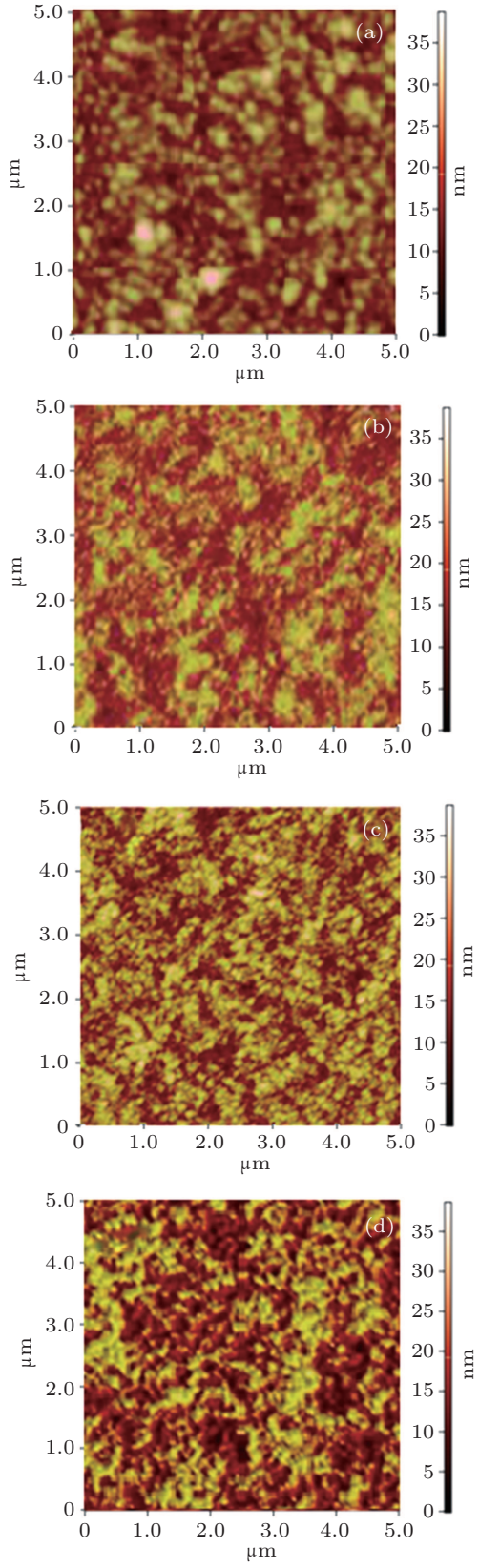


Fig. 4. (color online) AFM topographic images of PEDOT:PSS films (a) without glycerol treatment, (b) with 3% glycerol treatment, (c) with 6% glycerol treatment, and (d) with 9% glycerol.

in Fig. 4. The bright regions in Fig. 4 are hard domains corresponding to PEDOT, whereas the dark regions denote the soft structure arising from PSS.[22] With glycerol doping, the PEDOT areas increase, while the PSS areas decrease, which is consistent with the conclusion that co-solvent addition results in both the decrease of energy barrier for electric charge transport on the PEDOT chain and the increase of delocalization length.[17] Meanwhile, the surface root-mean-square roughness value of the PEDOT:PSS films increases from 2.83 nm for the untreated film to 4.66 nm for the film treated for 9% glycerol. The increase in the surface roughness value may induce an increase in the effective contact area between PEDOT:PSS and the active layer. Therefore, the enlarged effective contact area possibly results in the enhancement of J_{SC}.[21] Considering both the surface morphology and the current density, a critical doping ratio for PEDOT:PSS may exist as an optimum condition because the critical surface roughness may enable a more increased contact area between the PEDOT:PSS and perovskite layers. Moreover, rough surface facilitates light scattering and makes it possible to reflect the light back into the perovskite layer, thereby increasing light absorption.

3.4. Effect of glycerol doping on photo current of solar cells

Figure 5 shows the current density–voltage (J–V) curves of fabricated solar cells with various glycerol doping ratios on PEDOT: PSS under the illumination of AM 1.5 G (air mass 1.5 global), 100 mW·cm^{-2} and with the scan rate of 10 mV/100 ms. Detailed information about J_{SC}, V_{OC}, FF, and PCE which are calculated from the J–V curves, is presented in Table 1. It can be seen that the photovoltaic performance is dramatically enhanced for the solar cells with glycerol-treated PEDOT:PSS films. When a 3-wt% concentration glycerol is doped, the device J_{SC} increases from the original 14.85 mA·cm^{-2} (without glycerol doping) to 16.13 mA·cm^{-2}; the device PCE increases from 8.57% to 9.66%; then, when the glycerol doping concentration increases to 6 wt%, J_{SC} increased to 17.92 mA·cm^{-2}, FF increased to 72.39%, and PCE increased to 11.03%, and the cell J_{SC} and PCE increase respectively by 20.67% and 28.70% compared with those of the cell without glycerol doping. In addition, a reverse J–V scan is also given in Table 1. When a 6-wt% concentration glycerol is doped, the PCE of 11.41% is obtained and the hysteresis is negligible. The increase of the cell's J_{SC} mainly results from the performance change of the PEDOT: PSS thin film. The increase of electrical conductivity of glycerol doped PEDOT:PSS thin film leads to the decrease of the cell's series resistance; hole carriers in the device tend to flow from the perovskite layer to the ITO anode through the PEDOT:PSS thin film. However, excessive glycerol doping will result in the serious separation of PEDOT:PSS, as well as the occurrence of more defects, which are unfavorable for the hole transport.[22] Hence, in a device where 9% glycerol is doped into PEDOT: PSS, the J_{SC} and FF will both decrease.

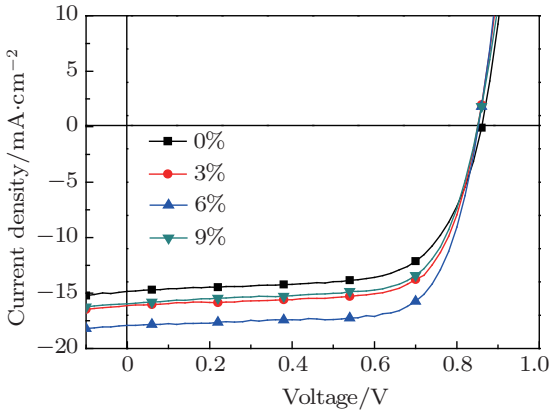


Fig. 5. (color online) Current density–voltage characteristics of perovskite solar cells with different doping ratios of glycerol under illumination of AM 1.5 G, 100 mW/cm^2.

Table 1. Conductivity values and performances of the cells with different amounts of glycerol content.

Scan direction	Glycerol content/wt%	Conductivity /S·cm^{-1}	V_{OC}/V	J_{SC}/mA·cm^{-2}	FF/%	PCE/%	R_S/Ω·cm^2	R_{SH}/Ω·cm^2
Forward	0	0.007	0.86	14.85	67.12	8.57	5.76	573.43
Forward	3	0.684	0.85	16.13	70.49	9.66	5.54	518.51
Forward	6	0.891	0.85	17.92	72.39	11.03	4.63	466.85
Forward	9	0.807	0.85	15.98	69.47	9.44	4.86	413.36
Reverse	0	0.007	0.86	15.19	67.35	8.80	5.35	617.24
Reverse	6	0.891	0.86	18.06	73.49	11.41	4.14	488.15

3.5. Effect of glycerol doping on dark currents of solar cells

To gain an in-depth understanding of the improvement in device performance after treating with different doping concentrations of glycerol, the J–V characteristics of the devices in dark conditions are measured and shown in Fig. 6. Scans are taken from −2.0 V to 2.0 V, and the device area-normalized data are plotted on a logarithmic scale. The dark state current curve of the cell can reflect the changes of the cell's series resistance (R_S) and shunt resistance (R_{SH}), and has an important reference value in evaluating the perovskite solar cell's

performance. The dark state curve of each solar cell can be divided into three regions:[24] in the low voltage region, there are symmetric small electric currents that are the leakage currents passing through the cell and are determined by R_{SH} in the cell. With the increase of voltage, the positive current increases in an exponential manner, indicating that the device has rectifying properties of diode; with the further increase of the voltage, due to the tunnel effect and restrictions on space charge transport, the growth rate of electric current decreases,[25] and the electric current, which is determined by the R_S in the cell at this time, is linearly related to with the voltage. The dark J–V curves in Fig. 6 show that the electric current increases after doping under forward bias, which means that the R_S of the doped device decreases and is in accordance with the overall increasing trend of the electrical conductivity of doped-PEDOT:PSS thin film. With the increase of glycerol-doping concentration under reverse bias, the reverse saturation current of the device gradually increases, indicating that the R_{SH} of the device decreases with the increase of glycerol-doping concentration, and the leakage current increases.

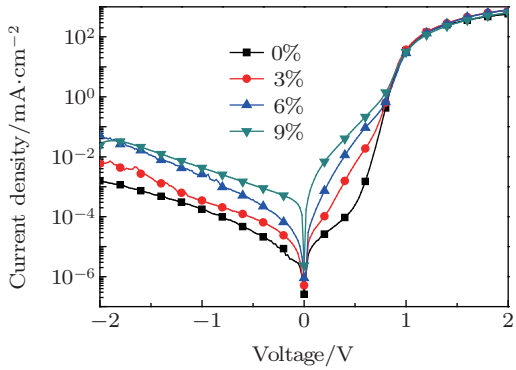


Fig. 6. (color online) Current density–voltage characteristics of perovskite solar cells with different doping ratios of glycerol in the dark.

4. Conclusions

In this paper, the influence of glycerol doped PEDOT:PSS thin film on the perovskite solar cell's photovoltaic performance is studied. The glycerol doping improves the electrical conductivity of the PEDOT:PSS thin film: when the glycerol doping concentration is 6%, the electrical conductivity reaches 0.89 S/cm, which is 127 times larger than that of un-doped film. The J_{SC} and PCE of the solar cell using a glycerol doped PEDOT:PSS anode buffer layer reach 17.92 mA·cm^{-2} and 11.03% respectively, which are raised by 20.67% and 28.70% compared with those of the un-doped device. It is due to the fact that the glycerol doping improves the electrical conductivity of PEDOT:PSS, resulting in the decrease of the total series resistance of the cell, and the hole carriers will flow from the perovskite layer to the ITO anode passing through the PEDOT:PSS thin film. Therefore, doping glycerol into the PEDOT:PSS is an effective method to improve the photovoltaic performance of perovskite solar cells.

References

[1] Wang W J, Ruderer M A, Metwalli En, Guo S A, Herzig E M, Perlich J and Muller-Buschbaum P 2015 *ACS Appl. Mater. Interfaces* **7** 8789
[2] Zhao Y, Liang C J, Zhang H M, Li D, Tian D, Li GB, Jing X P, Zhang W G, Xiao W K, Liu Q, Zhang F J and He Z Q 2015 *Energy Environ. Sci.* **8** 1256
[3] Yang X D, Chen H B, En B H and L Y 2015 *Acta Phys. Sin.* **64** 038404 (in Chinese)
[4] Shenvi N, Kempe J and Whaley K B 2003 *Phys. Rev. A* **67** 052307
[5] Zhang D F, Zheng L L, Ma Y Z, Wang S F, Bian Z Q, Huang C H, Gong Q H and Xiao L X 2015 *Acta Phys. Sin.* **64** 038803 (in Chinese)
[6] Yuan Y, Xu R, Xu H T, Hong F, Xu F and Wang L J 2015 *Chin. Phys. B* **24** 116302
[7] McGehee M D 2013 *Nature* **501** 323
[8] Kazim S, Nazeeruddin M K, Gratzel M and Ahmad S 2014 *Angew. Chem. Int. Ed.* **53** 2812
[9] Wang F Z, Tan Z A, Dai S Y and Li Y F 2015 *Acta Phys. Sin.* **64** 038401 (in Chinese)
[10] Sun S Y, Salim T, Mathews N, Duchamp M, Boothroyd C, Xing G C, Sum T C and Lam Y M 2014 *Energy Environ. Sci.* **7** 399
[11] Jeng J Y, Chiang Y F, Lee M H, Peng S R, Guo T F, Chen P and Wen T C 2013 *Adv. Mater.* **25** 3727
[12] Heo J H, Han H J, Kim D, Ahn T K and Im S H 2015 *Energy Environ. Sci.* **8** 1602
[13] Kim N, Kee S, Lee S H, Lee B H, Kahng Y H, Jo Y R, Kim B J and Lee K 2014 *Adv. Mater.* **26** 2268
[14] Lee S H, Sohn J S, KulkarnS B, Patil U M, Jun S C and Kim J H 2014 *Org. Electron.* **15** 3423
[15] Alemu D, Wei H Y, Ho K C and Chu C W 2012 *Energy Environ. Sci.* **5** 9662
[16] Vosgueritchian M, Lipomi D J and Bao Z N 2012 *Adv. Funct. Mater.* **22** 421
[17] Gong C, Yang H B, Song Q L, Lu Z S and Li C M 2012 *Solar Energy Materials & Solar Cells* **100** 115
[18] Ashizawa S, Horikawa R and Okuzaki H 2005 *Syn. Met.* **153** 5
[19] Nardes A M, Kemerink M, Kok M M, Vinken E, Maturova K and Janssen R A J 2008 *Org. Electron.* **9** 727
[20] Kim J Y, Jung J H, Lee D E and Joo J 2002 *Syn. Met.* **126** 311
[21] Shin K Y, Hong J Y and Jang J 2011 *Chem. Commun.* **47** 8527
[22] Hsiao Y Sh, Whang W T, Chen C P and Chen Y C 2008 *J. Mater. Chem.* **18** 5948
[23] Zhang F L, Gadisa A, Inganas O, Svensson M and Andersson M R 2004 *Appl. Phys. Lett.* **84** 3906
[24] Cruz C I, Reyes R M, Frutis M A, Rodriguez A G and Sandoval R L 2010 *Synth. Met.* **160** 1501
[25] Potscavage W J, Sharma J A and Kippelen B 2009 *ACC Chem. Res.* **42** 1758