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Realizing the ultimate goal of fully solution-processed organic solar cells: a compatible self-sintering method to achieve silver back electrode†

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It is commonly believed that the ultimate goal of high throughput production of organic solar cells (OSCs) is the fully solution process in the fabrication. While it is highly desirable to form metal back electrodes to complete OSCs by a solution process instead of high-vacuum evaporation to realize the goal, the complex solvents used in typical metal precursor solutions and the post-treatment required such as high-temperature annealing will easily damage active layers and degrade OSC performances. The power conversion efficiencies (PCE) for evaporation-free OSCs have only reached 8%. Besides, there are limited studies that provide clear evidence to successfully eliminate the solvent issue brought by the directly solution-processed metal back electrode. In this work, we demonstrate a compatible self-sintering approach to connect silver nanoparticles (NPs) into a high-quality back electrode. The as-achieved film exhibits a continuous crystal lattice, high purity, excellent conductivity and smooth morphology. Interestingly, since the self-sintering back electrode process is finished in a short time and uses a chemically compatible solvent, it will not degrade the organic active layer and favors high throughput OSCs fabrication. With the back electrode, the fully solution-processed OSCs achieve a PCE of 9.73% which is the highest reported PCE in evaporation-free OSCs to our best knowledge.

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1. Introduction

Organic solar cells (OSCs) show ever-increasing promise as a next generation energy source because of their high efficiency, environmental benignity, lightweight nature, flexibility, low cost, *etc.*^{1–4} Compared to high vacuum evaporated electrodes, solution-processed metal back electrodes have shown greater potential to realize fully solution-processed OSCs. Some works have investigated metal inks either in the form of metal nanoparticle ink or metal-organic precursor ink for solution-processed back electrodes. In general, additional post-treatments, such as high-temperature annealing,^{5–7} laser or microwave sintering⁶ and high-concentration inorganic salt sintering (electrolyte sintering),⁸ were required to ensure high conductivity and excellent film morphology. For instance, Tai and co-workers annealed their direct-written silver nanoparticles (Ag NPs) at 200 °C for 1 hour to get a highly conductive Ag line whose conductivity is as high as 25% of bulk silver.⁵ There is still concern that the post-treatments are too violent to the vulnerable organic active layers.

To lower the process temperature and ensure good film quality, it is common to add binders, complex solvents and other ingredients to the metal precursor solution of commercial inks. However, they will likely cause infiltration and contamination in the active layers and thus degrade the device efficiency. For example, Son and co-workers found that their OSCs were severely corroded by the solvent diffused from the printed back electrode under ambient conditions.⁹ The corresponding efficiency sharply dropped within hours. In order to protect the active layer from the complex solvent, an ultra-thick poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, 1 μm) layer should be deposited, which might have an adverse effect on device performance.⁹ Another approach to resolve the solvent issue is to deposit the bottom layers and back electrode separately, then assemble devices through a transformation or lamination process. Youn and co-workers separately fabricated bottom active layers and top layers including the printed back electrode and a PEDOT:PSS layer, and fabricated the device by laminating or transforming the top metal electrode onto the bottom part of the device.¹⁰ They finally achieved a PCE of 3.89%, comparable to the evaporated device (4.17%).¹⁰ Besides, some works have tried to deposit the metal back electrode beneath the active layer and finish the OSC by depositing a transparent electrode such as a Ag nanowire network on top of the device to eliminate the solvent issue. However, the as-deposited nanowires usually require post-treatment such as

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thermal annealing,¹¹ supersonic spray coating,¹² electroplating,¹³ flash-induced welding^{14,15} etc., which to a large extent increases fabrication complexity and some technologies are also destructive to the active layer.

Chemical sintering holds special promise since it is room temperature processable and flexible in solvent selection. Some chemical methods such as electrolyte sintering have been reported to sinter isolated Ag NPs into a conductive film.^{8,16} However, these chemical methods still have some challenges in the application to solar cells. Firstly, the employment of a high-concentration salt solution such as 0.1 mol L⁻¹ NaCl and MgCl₂ means the salts will be easily left in the electrode as impurities.¹⁶ Secondly, water is required as a solvent to ensure a high salt solubility, which would cause the dissolution of the hydrophilic bottom carrier transport layers (CTL). Simultaneously, the high surface-tension nature of water would also lead to a rough film, which may hinder the carrier transportation efficiency. So far, there are no reports that provide clear evidence showing the direct deposition of a solution-processed top back electrode without any solvent issues or interfacial issues. Resolving these issues is of great significance towards the manufacturing of OSCs.

In this work, we demonstrate a new direct electrode fabrication route to form high quality film. The approach not only addresses the solvent issue but also achieves a room temperature process. The pre-deposited well-dispersed Ag NPs will orient to match and integrate each other to become a conductive Ag back electrode under the stimulation of silver nitrate solution. Benefitting from a self-sintering behavior, the achieved film exhibits high purity (silver atom ratio higher than 99%), low sheet resistance (0.91 Ω sq⁻¹ for a 100 nm film) and low root mean square (RMS) roughness (2.298 nm). Remarkably, this approach can effectively work and sinter Ag NPs in most of the common solvents such as ethanol, dimethylformamide (DMF), ethyl acetate and anisole, which guarantees its wide application in photovoltaic and other fields. OSCs with inverted and conventional configurations have been demonstrated employing this solution-processed top back electrode, a similar carrier extraction and transportation properties to the evaporated counterparts are found. The device with an active layer of poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*])dithiophene))-*co*-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-*c*:4,5-*c'*])dithiophene-4,8-dione)] (PBDB-T):3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2',3'-*d'*]-*s*-indaceno[1,2-*b*:5,6-*b'*])dithiophene (IT-M) achieved a PCE of 9.73%. To the best of our knowledge, this is the highest efficiency among the reported evaporation-free OSCs, which makes a big step towards manufacturing of OSCs.

2. Results and discussion

2.1 Sheet resistance of the electrode

The Ag NPs used for forming the high-quality Ag back electrode with high conductivity and smooth morphology are synthesized through a fast AgNO₃ thermal reduction method with 10 minutes reaction.¹⁷ Fig. S1† confirms that the products are

mono-dispersed pure cubic Ag NPs with diameters around 6–10 nm (detailed discussion in the ESI†). In the new self-sintering approach, a layer of Ag NPs is pre-deposited on the substrate followed by dropping the silver nitrate solution on it. Fundamentally different from typical commercial Ag pastes which require high temperature or extrinsic solders or binders to ensure high cohesiveness and conductivity, yet could cause serious damage in organic photoactive films, the synthesized Ag NPs will spontaneously diffuse to match the (111) plane and interconnect with each other to form the high-quality back electrode. Interestingly, since the self-sintering process will complete in a very short time using chemically compatible solvents, the approach will not degrade the organic active layer and favor high throughput OSCs fabrication. Details of the characterization and the mechanism of the high-quality film formation for the compatible self-sintering approach will be described.

Fig. 1a shows the film sheet resistance as a function of sintering time. It reveals that a 26.8 nm Ag NP electrode after 10 s sintering can achieve a sheet resistance of 6.9 Ω sq⁻¹, which is far lower than that of the film without treatment (>100 Ω sq⁻¹). Further increasing the time leads to a slight reduction in sheet resistance to 4.2 Ω sq⁻¹. The results suggest that the sintering process is exceedingly fast compared to many other Ag NPs sintering methods such as electrolyte sintering (12 h,⁸ 10 s (ref. 16)), thermal sintering (20 min,¹⁸ 10 min,¹⁹ 3 min (ref. 11)), UV-curing (1 min (ref. 9)), etc. In addition, AgNO₃ in different solvents with a variety of polarities is favorable in our approach, indicating its flexibility and wide adaptability. As shown in Fig. 1b, the sheet resistances of the Ag NP electrode show an incredible decrease from over 100 Ω sq⁻¹ to less than 5 Ω sq⁻¹ after treatment (details in Table S1 in the ESI†). Especially in ethanol solution, a 100 nm Ag electrode delivers a sheet resistance of 0.91 Ω sq⁻¹, which is comparable to the evaporated Ag electrode (0.48 Ω sq⁻¹). Since most of the organic active materials can be dissolved in aromatic solvents with relatively low polarity such as chlorobenzene, ethanol can be an appropriate choice for electrode deposition in OSCs.

2.2 Crystal structure, morphology and chemical composition evolution of the solution process

We then further investigate the electrode formation process using ethanol as a model solvent. Fig. 2a displays the XRD patterns of the electrodes in the pristine state and after the treatment of AgNO₃ solutions with different concentrations. The sintering process has not changed the crystal structure of the electrode. All of them exhibit four peaks at 38.1°, 44.3°, 64.4° and 77.5°, which confirms their cubic silver crystal structure. After sintering, the full width at half maximum (FWHM) values of the peak indexed to the (111) plane has decreased from 2.38° to 0.68° (2 θ). Such a conspicuous decrease suggests a significant expansion of the particle size. Fig. 2b and c compare the surface morphology of the electrode before and after sintering, respectively. A morphology change from small isolated NPs to connected continents is clearly captured after sintering. Moreover, the sintered electrode presents a low root mean square

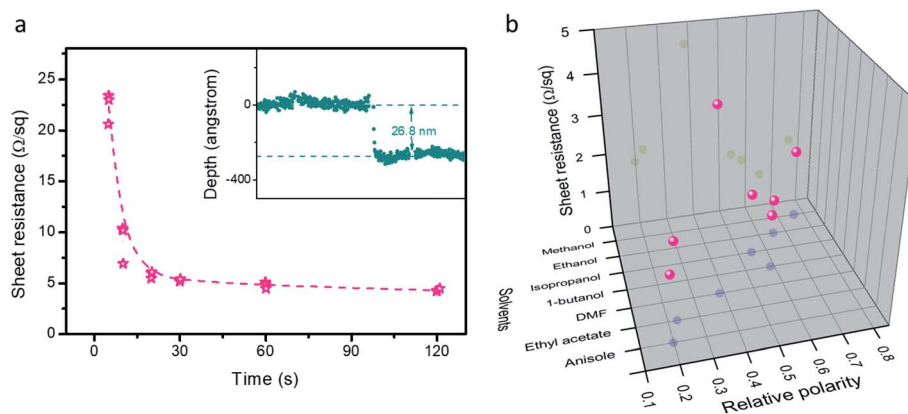


Fig. 1 (a) Film sheet resistance as a function of sintering time. The inset shows the thickness of the Ag electrode. (b) Film sheet resistance after the sintering of silver nitrite in different solvents.

roughness (R_{RMS}) of 2.298 nm, which is comparable to the evaporated Ag electrode (2.191 nm, Fig. 2d and e). The extracted surface height histogram figure (Fig. 2f) shows similar height distributions for the two electrodes, suggesting the solution-processed electrode is favourable for OSCs fabrication.

Fig. 2g and h present the TEM images of the electrode before and after solution treatment, respectively. Before sintering, NPs with diameters of 6–10 nm and lattice distance of 2.36 Å (111 plane) are shown. However, a cluster of well-bonded silver comes into being after the solution process. The white dashed lines in Fig. 2h mark the interface of two particles astride which (111) planes of cubic silver are shown with a misorientation angle of 21° . Such a small

misorientation angle can be ascribed to the lattice planes tending to orient to match to each other in the solution.²⁰ The results imply that the chemical sintering method can result in well-matched lattices between particles.²¹

AgNO_3 has been reported to weld Ag nanowires by reducing the AgNO_3 to become Ag solders. The solders will accumulate at the junction to connect the Ag nanowires.^{22,23} However, in this work, extra solders are neither required nor detected between the Ag NPs. The particles will conduct self-sintering when stimulated by the solution, which ensures a high crystallinity of the resultant film. In addition, the ionic state of the chemicals is essential to promote the breakage of the coordination bond between the ligand and particles.¹⁶

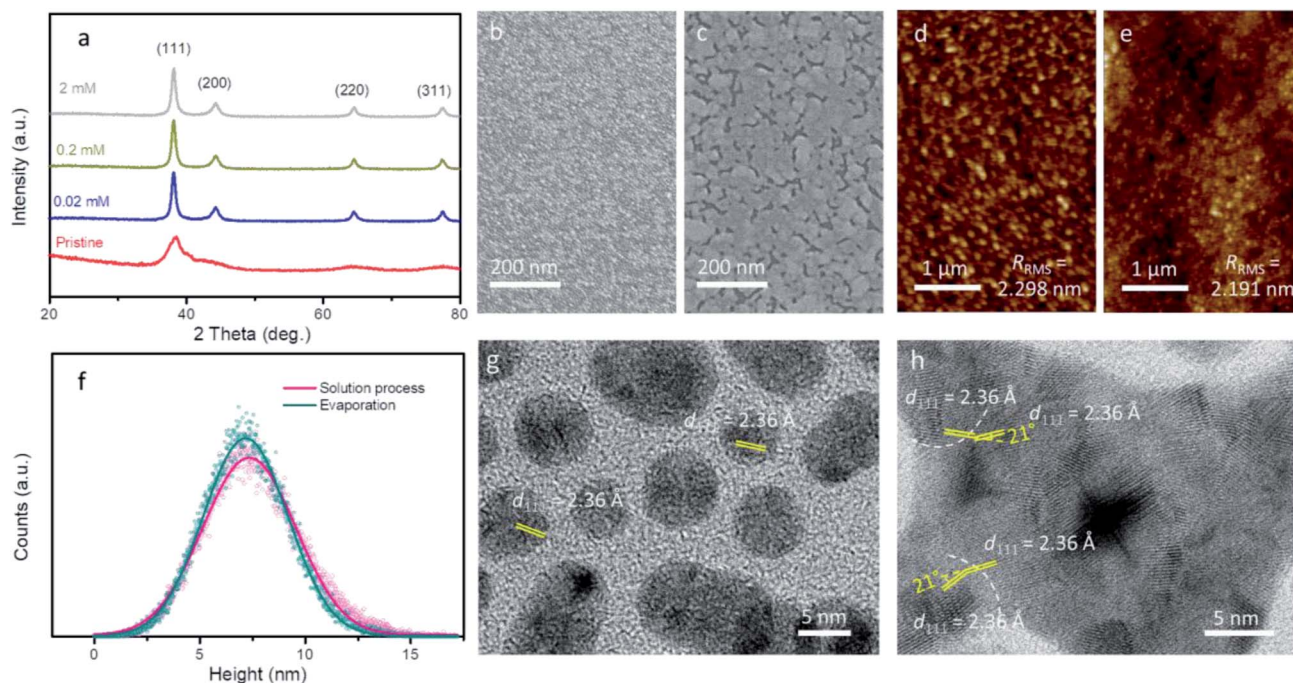


Fig. 2 (a) XRD pattern of Ag electrode in pristine state or after the treatment of AgNO_3 solution at different concentrations. SEM images of Ag electrodes in (b) pristine and (c) sintered states. AFM images of (d) sintered state of solution-processed Ag electrode, and (e) evaporated Ag electrode; (f) extracted surface height histograms. HR-TEM images of Ag NPs (g) before and (h) after chemical sintering.

X-ray photoelectron spectroscopy (XPS) has been further carried out to monitor the binding energy evolution after chemical treatment. Fig. 3a and b compare the core level Ag 3d and N 1s XPS spectra of the electrodes before and after sintering. The corresponding XPS survey spectra can be found in Fig. S3 in the ESI.† As shown in the spectrum of the sintered electrode (Fig. 3a), a pair of peaks located at 374.4 eV and 368.4 eV are deconvoluted, which can be well indexed to $\text{Ag}^0 3d_{3/2}$ and $\text{Ag}^0 3d_{5/2}$ of bulk silver.^{24–26} The other two small peaks sited at 375.5 eV and 369.5 eV should be indexed to the nitrogen coordinated silver ($\text{Ag-N } 3d_{3/2}$ and $\text{Ag-N } 3d_{5/2}$).²⁷ Compared to the pristine electrode, the sintered one shows a peak shift of around 0.4 eV towards lower binding energy, which can be ascribed to the size effect. Compared to the bulk materials, a shift of 0.5–2.0 eV is possible for small particles because of the depletion of electrons in the valence band with the decreasing particle size.^{25,28} Besides, the ratio of the Ag–N declines from 8.6% to 3.5% after sintering (Table S2, ESI†). Therefore, we can confirm that the Ag–N coordination bond is broken during the solution process. The peaks at 398.2 eV and 399.6 eV can be assigned to N–C (ref. 21) and N–Ag (ref. 29) (Fig. 3b). The atom ratio of N coordinated to silver also shows

a decrease (Fig. S4, ESI†). Importantly, the absence of the NO_3^- signal (406.6 eV) proves the AgNO_3 has been degraded into silver after sintering and no excess impurities are left in the electrode (Fig. S5, ESI†). The core level C 1s and O 1s XPS spectra are provided in Fig. S6.† The deconvoluted peaks can be well indexed to C–C bond,³⁰ chemisorbed oxygen (O1) and physical or chemisorbed water at the surface (O2).^{31,32}

We are therefore ready to propose a plausible mechanism for the high-quality electrode formation process. Generally, it takes two steps to make this back electrode. Firstly, the synthesized Ag NPs in solution were spin-coated on the carrier transport layer to form a smooth, uniform but disconnected Ag NPs film. Secondly, 100 μL of silver nitrate (AgNO_3 , different concentrations in ethanol) was dropped on the pre-deposited Ag NPs film. Then, the samples were kept for 30 s. During this process, the coordinate bond between the Ag NPs and their surface ligand will break under the effect of the ions in the solution. The bare Ag NPs would be exposed accordingly. Then, the exposed grain boundary or surface of the NPs will diffuse to match each other with the lattice of the (111) plane.²¹ Interestingly, an extremely low concentration of AgNO_3 ($2 \times 10^{-5} \text{ mol L}^{-1}$) can facilitate the

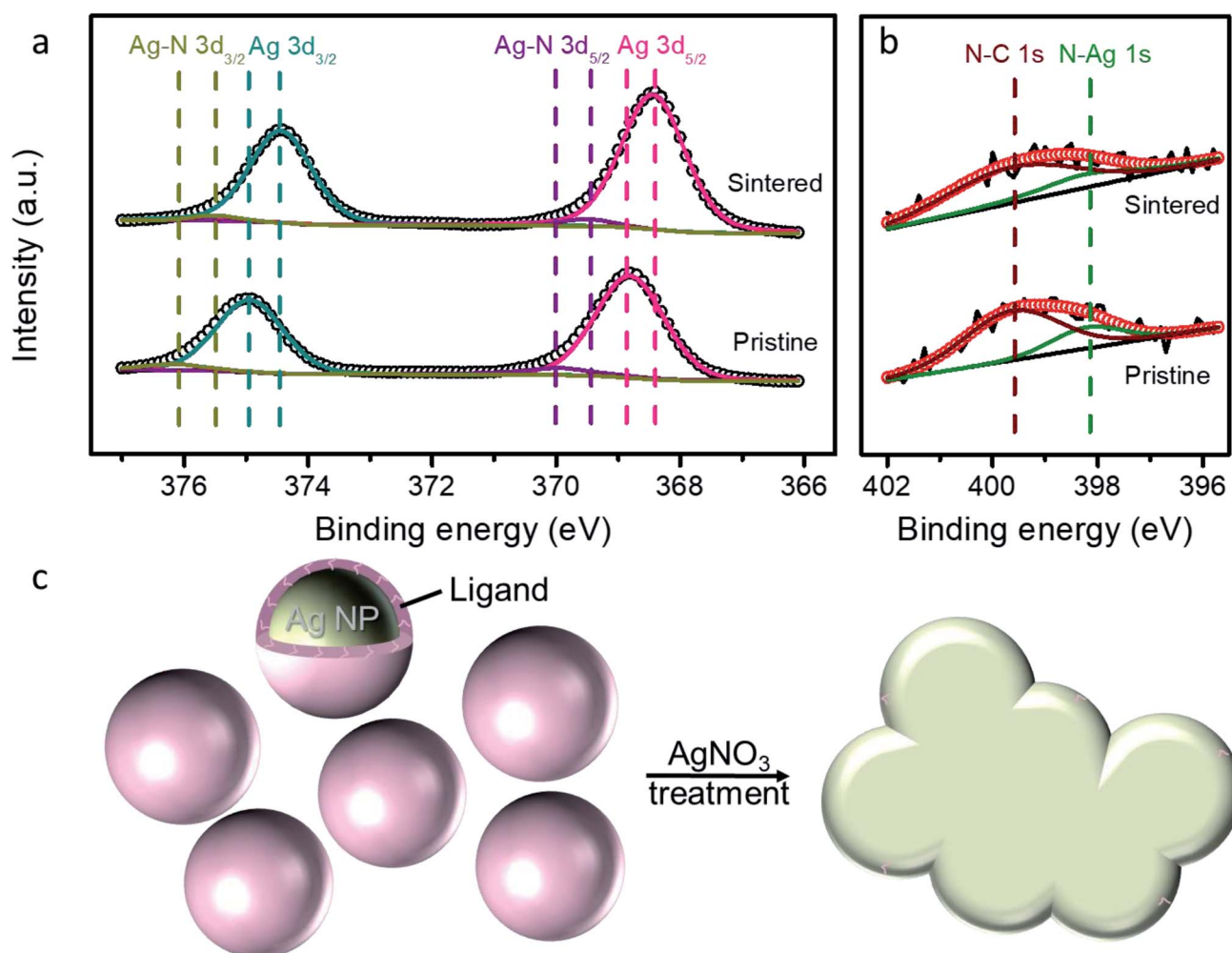


Fig. 3 Core-level (a) Ag 3d and (b) N 1s XPS spectra of the electrodes in pristine and sintered states. (c) Schematic illustration of the chemical sintering mechanism.

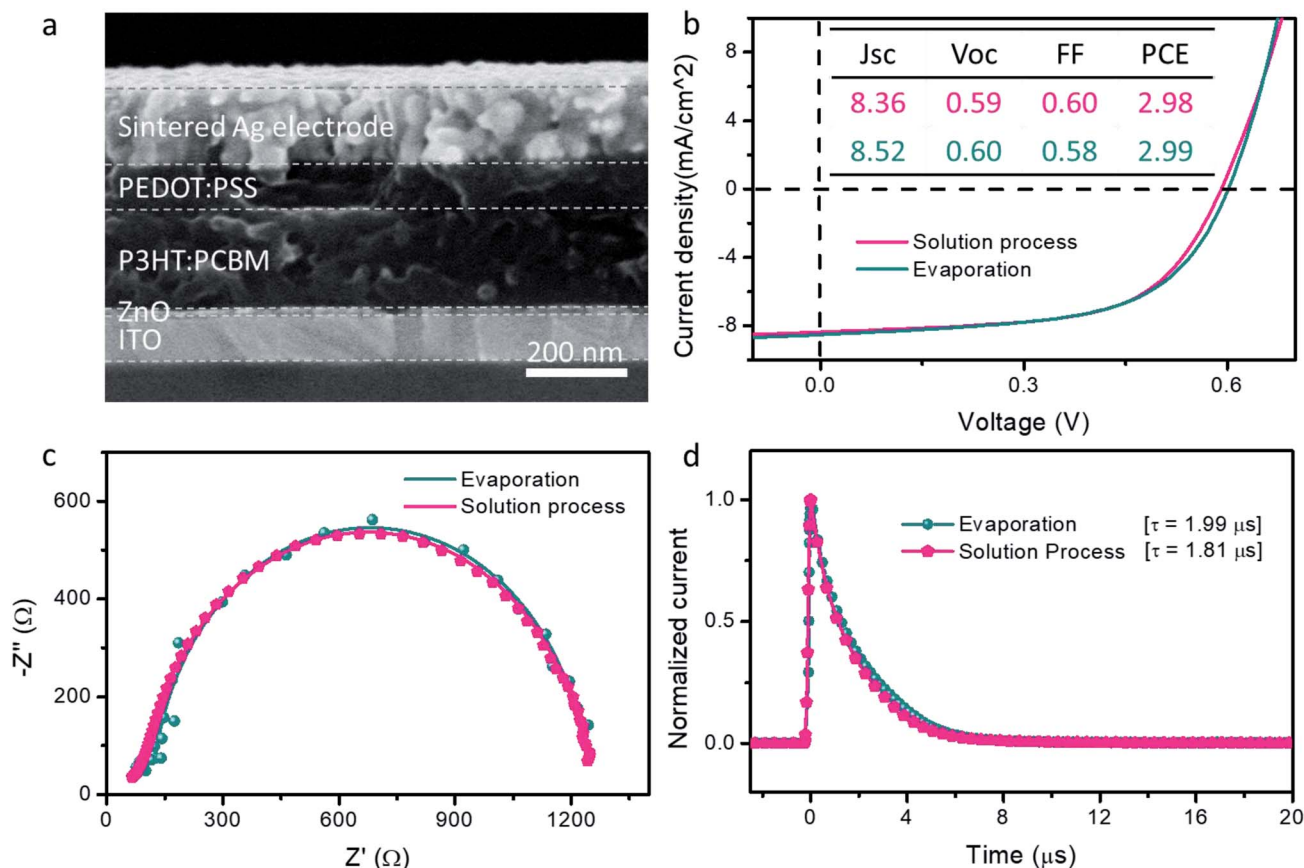


Fig. 4 (a) The cross-sectional SEM image of the fully solution-processed device. (b) The J–V curves, (c) impedance spectrum and (d) transient photocurrent measurement of the devices with a solution-processed and evaporated silver back electrode.

merging of the particles and the sintering can be finished in a short time. The schematic illustration of this process is shown in Fig. 3c. Finally, the device is blown with nitrogen and left in a glove box for 1 hour or 80 °C heating for 10 min to drive away excess solvent. In this procedure, the AgNO_3 left in the electrode will easily degrade into silver and oxynitride gas. Therefore, a pure and high-quality back electrode is formed.

It is noteworthy that oleylamine plays a critical role in the electrode formation. Firstly, its short carbon backbone and amino end group limit the shape and diameter of the Ag NPs, thus guaranteeing a compact stacking of the nanoparticles in the deposition process. Secondly, benefitting from its excellent dispersity, the Ag NPs can be well spread and distributed on the substrate without causing terrible aggregation, which is essential for the electrode conductivity. Finally, it provides a moderate coordinate force with the Ag NPs. Therefore, it can protect the NPs from oxidation and simultaneously is easy to break in the solution, which contributes to the good inter-particle connection and excellent electrical properties of the electrodes.

2.3 Performances of the OSCs

The critical issue that a solution method can result in is the dissolution of underneath layers of the OSCs and poor electrical contact, which are likely to affect the interfacial resistance and

carrier transportation. To address the issue, we fabricate a well-recognized inverted OSC configuration of ITO/ZnO/poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl- C_{61} -butyric acid methyl ester (P3HT:PCBM)/PEDOT:PSS/Ag to evaluate the photoelectrical properties and the compatibility of the solution-processed Ag NP electrode. The cross-sectional SEM image of the device is shown in Fig. 4a. A fine and uniform Ag back electrode is deposited on the top of the device. Besides, the boundary between the PEDOT:PSS and nanoparticles electrode is well defined (Fig. S7†), which confirms the carrier transport layer is well preserved during the solution process and ensures great interfacial properties of the electrode. Electrochemical impedance spectra of devices with a solution-processed or evaporated Ag electrode are given in Fig. 4c. Both of the EIS spectra present two semicircles indicating a carrier transport resistance (R_1) and a charge recombination resistance (R_2).³³ Fig. S8 in the ESI† presents the equivalent circuit of the corresponding EIS spectra. It is shown that the spectra can be well fitted by the provided equivalent circuit. An R_1 of 61.87 Ω and an R_2 of 1143 Ω are extracted for the device with a solution-processed electrode, which are similar to its evaporated control device with an R_1 of 60 Ω and an R_2 of 1123 Ω. This result suggests the electrical contact between the solution-processed electrode and the bottom HTL is as excellent as the evaporated one. In addition, we further employed transient photocurrent measurements to

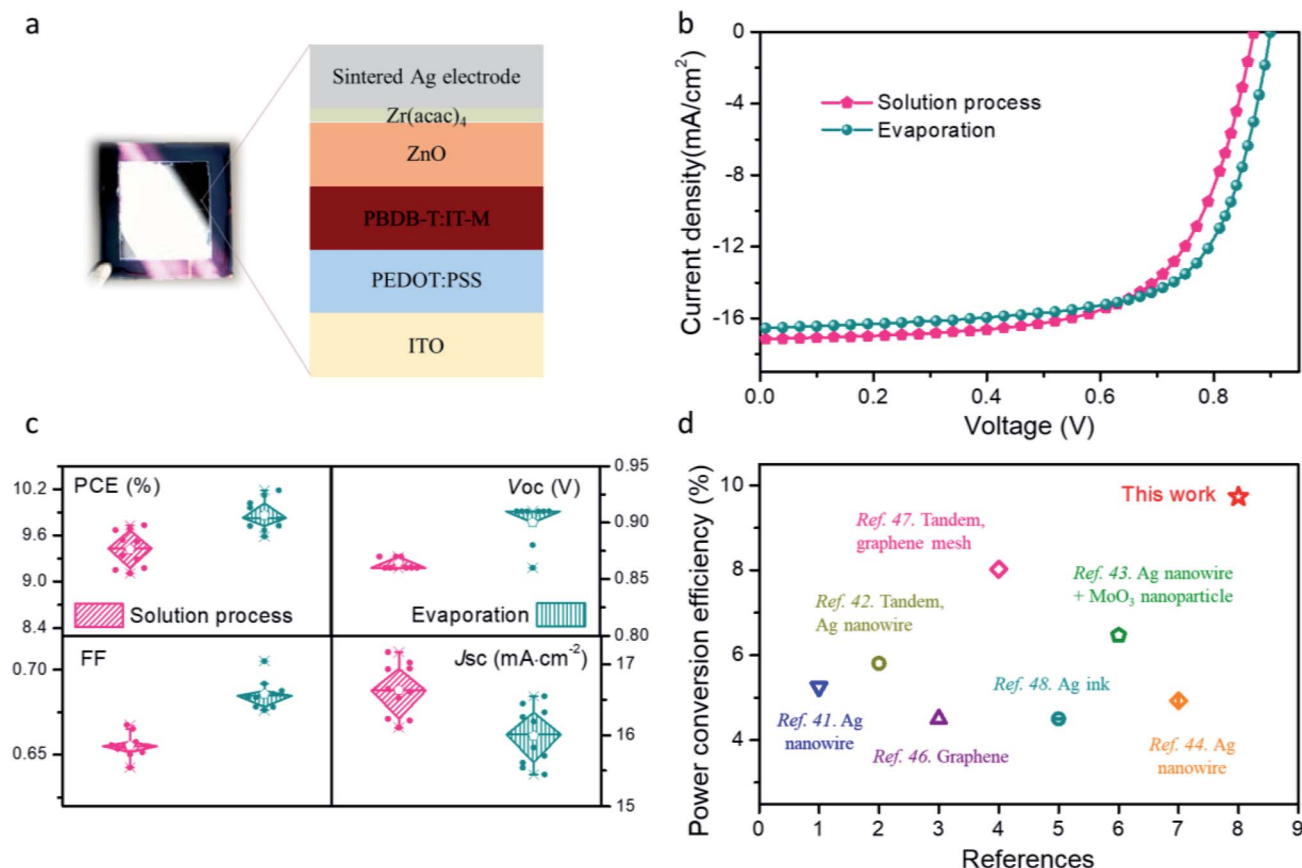


Fig. 5 (a) Image of the device with a solution-processed silver electrode and its schematic illustration. (b) The current density–voltage curve and (c) curve parameters with distribution statistics of the devices with a solution-processed or evaporated silver electrode. (d) The comparison of power conversion efficiency between this work and other evaporation-free devices.

characterize the carrier extraction property of the devices (Fig. 4d). A charge extraction time of $1.81 \mu\text{s}$ is fitted for the fully solution-processed device, which is slightly lower than the $1.99 \mu\text{s}$ of the evaporated one and indicates a slightly faster charge extraction. All of these results confirm that there is no visible materials dissolution nor device destruction after the solution deposition of the Ag electrode. Additionally, the charge transportation and electrical contact of the solution-processed device are almost the same as the device with an evaporated electrode, suggesting its excellent compatibility. Fig. 4b compares the current density–voltage (J – V) curves of both devices with the solution-processed or evaporated electrode under 1 simulated sun light illumination (100 mW cm^{-2}). The fully solution-processed device presents a PCE of 2.98% with an open-circuit voltage (V_{oc}) of 0.59 V, a short-circuit current density (J_{sc}) of 8.36 mA cm^{-2} and a fill factor (FF) of 0.60, which is similar to its evaporated counterpart. It is important to note that the exhibited photovoltaic performance is better than most of the recently reported P3HT:PCBM devices with a directly solution-processed opaque Ag electrode (Fig. S9 and Table S3, ESI†).^{9,11,18,34–40}

OSCs with a normal device configuration of ITO/PEDOT:PSS/PBDB-T:IT-M/ZnO/ $\text{Zr}(\text{acac})_4$ /Ag are also constructed to investigate the wide applicability of this solution-processed electrode.

Similarly, the Ag NPs back electrode is uniformly deposited on top of the solar cells without causing any obvious destruction (Fig. 5a). As shown in Fig. 5b, a PCE of 9.73% is characterized for the solution-processed device with a V_{oc} of 0.87 V, J_{sc} of 17.17 mA cm^{-2} and FF of 0.65. The results are comparable to its evaporated counterpart with a PCE of 10.19%, V_{oc} of 0.90 V, J_{sc} of 16.55 mA cm^{-2} and FF of 0.68. Fig. 5c and Table S4† display the solar cell parameters of the devices finished by the solution process or evaporation. A small error range of 0.2% for both devices is shown, which suggests that the performance among different solution-processed devices has little deviation and the result is highly reproducible. To the best of our knowledge, this is the highest PCE compared to other reported evaporation-free devices that employ a solution-processed electrode such as Ag nanowire,^{41–45} graphene^{46,47} and Ag ink⁴⁸ (Fig. 5d).

3. Conclusion

In summary, a new approach to self-sintering mono-dispersed Ag NPs into a well-connected/integrated Ag film at room temperature is proposed and demonstrated. Interestingly, during the sintering process, the grain boundary of the NPs will autonomously orient to match to each other in the proposed solution, which leads to a good particle interface

interconnecting to form the back electrode. The resultant film exhibits excellent quality with a sheet resistance of $0.91 \Omega \text{ sq}^{-1}$ and an RMS roughness of 2.298 nm, which are comparable to the conventionally evaporated Ag electrode. Importantly, the device constructed by this solution-processed back electrode delivers a carrier extraction and transportation properties as good as its evaporated counterpart. The results imply that this method successfully eliminates the critical solvent and interfacial issues during the solution process. We have also unveiled the formation mechanism of the efficient solution-processed Ag NPs based electrode. An OSC with a PCE of 9.73% has been achieved, which outperforms the other reported evaporation-free devices. It is noteworthy that our electrode can be deposited on different carrier transport layers and is suitable for fullerene and non-fullerene based OSCs with either conventional or inverted configuration. In addition, the sintering also favors the use of various solvents. These facts imply that the solution-processed electrode is applicable to other optoelectronic devices with a layered structure such as light emitting diodes (LEDs) and photodetectors. This work not only offers a new approach to resolve the solvent and interfacial issues brought by the solution process for top back electrodes but also paves the way for all solution-based high-throughput production of the next generation of power devices.

4. Experimental section

4.1 Chemicals

Silver nitrate (AgNO_3 , 99%), zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2$, 98%), ethanolamine (99.9%), methanol (99.8%), dichlorobenzene (DCB, 99.8%) and Triton X100 (98%) were purchased from Sigma-Aldrich. Oleylamine (98%), *n*-octane (99%), ethyl acetate (99.5%) and anisole (99%) were purchased from FineLab. *n*-Hexane (GR) was purchased from IL. Ethanol (99.5%) and 1-butanol (99.4%) were purchased from J&K. Dimethylformamide (99%) and isopropanol (99.8%) were purchased from Acros. P3HT, PC_{61}BM , PBDB-T and IT-M were purchased from Solarmer Co., Ltd. PEDOT:PSS (Baytron Al4083) was purchased from H.C. Starck GmbH, Germany. 1,8-Diiodooctane (DIO, >95.0%) was purchased from Tokyo Chemical Industry Co., Ltd. (TCI).

4.2 Synthesis of Ag NPs

Ag NPs were synthesized by thermal reduction of AgNO_3 .¹⁷ Firstly, oleylamine (15 mL) was added into a round-bottom flask (100 mL) and was pre-heated in an oil bath at 192 °C for 30 min. Then, silver nitrate (0.75 g) was added into the solution and was reacted for 10 min. The product was cooled to room temperature and washed with ethanol 5 times. Finally, the product was vacuum dried for 4 hours and re-dispersed in hexane and octane with a ratio of 1 : 1.

4.3 Ag film formation and device fabrication

ITO coated glass substrates were cleaned in turn in deionized water, acetone and ethanol under ultrasonication for 15 min. For devices with an inverted configuration, ZnO solution was prepared following a reported sol-gel strategy.⁴⁹ The ZnO

solution was spin-coated on the cleaned ITO substrate at 4000 rpm and the substrates were annealed at 200 °C for 15 min in air. Then, P3HT: PC_{61}BM (20 : 20 mg mL^{-1} in dichlorobenzene) solution was spin-coated onto the pre-deposited ZnO layer followed by 1 h slow-growth and 130 °C annealing for 10 min. The PEDOT:PSS (Baytron AI 4083, with 1 vol% addition of Triton) was deposited on top of P3HT:PCBM followed by 150 °C annealing for 5 min. After that, Ag NPs were spin coated on the PEDOT:PSS film followed by dropping $2 \times 10^{-5} \text{ mol L}^{-1}$ AgNO_3 (in ethanol) on it for 30 seconds. Finally, the device is blown with nitrogen and then left in a glove box for 1 hour or 80 °C heating for 10 min to drive away excess solvent. The thickness of the Ag NP back electrode is around 140 nm. For devices with a conventional structure, a layer of PEDOT:PSS was deposited on the cleaned ITO with a thickness of around 40 nm. PBDB-T:IT-M (10 : 10 mg mL^{-1} in chlorobenzene with 1 vol% addition of DIO) was spin-coated on top of the PEDOT:PSS layer with a thickness of 100 nm followed by 160 °C annealing for 30 min. After that, ZnO NPs (15 mg mL^{-1} in 1-butanol, synthesized according to ref. 50) and $\text{Zr}(\text{acac})_4$ (2 mg mL^{-1} in ethanol) were deposited on the active layer, in turn. Finally, a layer of the solution-processed Ag electrode was formed as mentioned above. For the device with an evaporated Ag electrode, it was finished by thermally evaporating a layer of 120 nm thick Ag.

4.4 Material and device characterizations

The morphology, microstructures and compositions of the electrodes or devices were analyzed using SEM (Hitachi S-4800), TEM (Philips Tecnai G2 20 S-TWIN), AFM (NT-MDT NTEGRA), XRD (Cu $K\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$, Bruker D2 PHASER) and XPS (Al $K\alpha$ X-ray source, Physical Electronics PHI 5802). The sheet resistance was tested using a SIGNATONE 4-point probe measurement system. Layer thickness was obtained using a D-500 Stylus Profilometer. *J-V* curves were measured using a Keithley 2635 sourcemeter and ABET AM 1.5G solar simulator. The EIS was conducted using an electrochemical station (Zahner, Zennium Pro) with a frequency range from 100 Hz to 1 MHz and an AC amplitude of 10 mV under light illumination with a white LED array (100 mW cm^{-2}). Transient photocurrent measurement was carried out under a 532 nm 6 ps pulse width laser (130 μJ per pulse at 50 Hz) and monitored using a 4 GHz Keysight MSO9404A digital oscilloscope.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 T. Kim, S. Kang, J. Heo, S. Cho, J. W. Kim, A. Choe, B. Walker, R. Shanker, H. Ko and J. Y. Kim, *Adv. Mater.*, 2018, **30**, 1800659.
- 2 Z. Li, L. Ying, P. Zhu, W. Zhong, N. Li, F. Liu, F. Huang and Y. Cao, *Energy Environ. Sci.*, 2019, **12**, 157.
- 3 B. Guo, W. Li, G. Luo, X. Guo, H. Yao, M. Zhang, J. Hou, Y. Li and W.-Y. Wong, *ACS Energy Lett.*, 2018, **3**, 2566.
- 4 Y. Xie, W. Wang, W. Huang, F. Lin, T. Li, S. Liu, X. Zhan, Y. Liang, C. Gao, H. Wu and Y. Cao, *Energy Environ. Sci.*, 2019, **12**, 3556.
- 5 Y.-L. Tai and Z.-G. Yang, *J. Mater. Chem.*, 2011, **21**, 5938.
- 6 J. Niittynen, R. Abbel, M. Mäntysalo, J. Perelaer, U. S. Schubert and D. Lupo, *Thin Solid Films*, 2014, **556**, 452.
- 7 B. Y. Ahn, E. B. Duoss, M. J. Motala, X. Guo, S.-I. Park, Y. Xiong, J. Yoon, R. G. Nuzzo, J. A. Rogers and J. A. Lewis, *Science*, 2009, **323**, 1590.
- 8 M. Layani, M. Grouchko, S. Shemesh and S. Magdassi, *J. Mater. Chem.*, 2012, **22**, 14349.
- 9 H. J. Son, S. H. Kim and D. H. Kim, *Adv. Energy Mater.*, 2017, **7**, 1601289.
- 10 H. Yoon, T. Lee and L. J. Guo, *Energy Environ. Sci.*, 2014, **7**, 2764.
- 11 J. Krantz, K. Forberich, P. Kubis, F. Machui, J. Min, T. Stubhan and C. J. Brabec, *Org. Electron.*, 2015, **17**, 334.
- 12 A. G. Ricciardulli, S. Yang, G.-J. A. H. Wetzelaer, X. Feng and P. W. M. Blom, *Adv. Funct. Mater.*, 2018, **28**, 1706010.
- 13 H. Kang, S.-J. Song, Y. E. Sul, B.-S. An, Z. Yin, Y. Choi, L. Pu, C.-W. Yang, Y. S. Kim, S. M. Cho, J.-G. Kim and J. H. Cho, *ACS Nano*, 2018, **12**, 4894.
- 14 J. H. Park, G.-T. Hwang, S. Kim, J. Seo, H.-J. Park, K. Yu, T.-S. Kim and K. J. Lee, *Adv. Mater.*, 2017, **29**, 1603473.
- 15 C. Lee, Y. Oh, I. S. Yoon, S. H. Kim, B.-K. Ju and J.-M. Hong, *Sci. Rep.*, 2018, **8**, 2763.
- 16 Y. Long, J. Wu, H. Wang, X. Zhang, N. Zhao and J. Xu, *J. Mater. Chem.*, 2011, **21**, 4875.
- 17 D. Wang, T. Xie, Q. Peng and Y. Li, *J. Am. Chem. Soc.*, 2008, **130**, 4016.
- 18 D. Angmo, J. Sweelssen, R. Andriessen, Y. Galagan and F. C. Krebs, *Adv. Energy Mater.*, 2013, **3**, 1230.
- 19 Y. Wu, Y. Li and B. S. Ong, *J. Am. Chem. Soc.*, 2007, **129**, 1862.
- 20 P. Peng, L. Liu, A. P. Gerlich, A. Hu and Y. N. Zhou, *Part. Part. Syst. Charact.*, 2013, **30**, 420.
- 21 P. Peng, L. Li, W. Guo, Z. Hui, J. Fu, C. Jin, Y. Liu and Y. Zhu, *J. Phys. Chem. C*, 2018, **122**, 2704.
- 22 H. Lu, D. Zhang, J. Cheng, J. Liu, J. Mao and W. C. H. Choy, *Adv. Funct. Mater.*, 2015, **25**, 4211.
- 23 H. Lu, D. Zhang, X. Ren, J. Liu and W. C. H. Choy, *ACS Nano*, 2014, **8**, 10980.
- 24 S. Calderon V, R. E. Galindo, N. Benito, C. Palacio, A. Cavaleiro and S. Carvalho, *J. Phys. D: Appl. Phys.*, 2013, **46**, 325303.
- 25 I. Lopez-Salido, D. C. Lim and Y. D. Kim, *Surf. Sci.*, 2005, **588**, 6.
- 26 S. W. Han, Y. Kim and K. Kim, *J. Colloid Interface Sci.*, 1998, **208**, 272.
- 27 G. Xue, Q. Dai and S. Jiang, *J. Am. Chem. Soc.*, 1988, **110**, 2393.
- 28 V. Vijayakrishnan, A. Chainani, D. D. Sarma and C. N. R. Rao, *J. Phys. Chem.*, 1992, **96**, 8679.
- 29 L. Duan, P. Wang, X. Yu, X. Han, Y. Chen, P. Zhao, D. Li and R. Yao, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4092.
- 30 L. F. E. Machogo, P. Tetyana, R. Sithole, S. S. Gqoba, N. Phao, M. Airo, P. M. Shumbula, M. J. Moloto and N. Moloto, *Appl. Surf. Sci.*, 2018, **456**, 973.
- 31 D. Ouyang, J. Xiao, F. Ye, Z. Huang, H. Zhang, L. Zhu, J. Cheng and W. C. H. Choy, *Adv. Energy Mater.*, 2018, **8**, 1702722.
- 32 H. Yoon, D. Kim, M. Park, J. Kim, J. Kim, W. Srituravanich, B. Shin, Y. Jung and S. Jeon, *J. Phys. Chem. C*, 2018, **122**, 12114.
- 33 J. Cheng, H. Zhang, Y. Zhao, J. Mao, C. Li, S. Zhang, K. S. Wong, J. Hou and W. C. H. Choy, *Adv. Funct. Mater.*, 2018, **28**, 1706403.
- 34 G. Polino, S. Shanmugam, G. J. P. Bex, R. Abbel, F. Brunetti, A. Di Carlo, R. Andriessen and Y. Galagan, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2325.
- 35 T. M. Eggenhuisen, Y. Galagan, A. F. K. V. Biezemans, T. M. W. L. Slaats, W. P. Voorthuizen, S. Kommeren, S. Shanmugam, J. P. Teunissen, A. Hadipour, W. J. H. Verhees, S. C. Veenstra, M. J. J. Coenen, J. Gilot, R. Andriessen and W. A. Groen, *J. Mater. Chem. A*, 2015, **3**, 7255.
- 36 E. Georgiou, A. Savva, M. Neophytou, F. Hermerschmidt, T. Demosthenous and S. A. Choulis, *Appl. Phys. Lett.*, 2014, **105**, 233901.
- 37 B. R. Patil, S. Shanmugam, J.-P. Teunissen and Y. Galagan, *Org. Electron.*, 2015, **21**, 40.
- 38 D. Angmo, H. F. Dam, T. R. Andersen, N. K. Zawacka, M. V. Madsen, J. Stubager, F. Livi, R. Gupta, M. Helgesen, J. E. Carlé, T. T. Larsen-Olsen, G. U. Kulkarni, E. Bundgaard and F. C. Krebs, *Energy Technol.*, 2014, **2**, 651.
- 39 Y. Galagan, S. Shanmugam, J. P. Teunissen, T. M. Eggenhuisen, A. F. K. V. Biezemans, T. Van Gijsegheem, W. A. Groen and R. Andriessen, *Sol. Energy Mater. Sol. Cells*, 2014, **130**, 163.
- 40 J. Kim, N. Duraisamy, T.-M. Lee, I. Kim and K.-H. Choi, *Mater. Res. Bull.*, 2015, **70**, 412.
- 41 S. Strohm, F. Machui, S. Langner, P. Kubis, N. Gasparini, M. Salvador, I. McCulloch, H. J. Egelhaaf and C. J. Brabec, *Energy Environ. Sci.*, 2018, **11**, 2225.
- 42 F. Guo, N. Li, V. V. Radmilović, V. R. Radmilović, M. Turbiez, E. Spiecker, K. Forberich and C. J. Brabec, *Energy Environ. Sci.*, 2015, **8**, 1690.
- 43 L. K. Jagadamma, H. Hu, T. Kim, G. O. N. Ndjawa, A. E. Mansour, A. El Labban, J. C. D. Faria, R. Munir, D. H. Anjum, M. A. McLachlan and A. Amassian, *Nano Energy*, 2016, **28**, 277.
- 44 G. Ji, Y. Wang, Q. Luo, K. Han, M. Xie, L. Zhang, N. Wu, J. Lin, S. Xiao, Y.-Q. Li, L.-Q. Luo and C.-Q. Ma, *ACS Appl. Mater. Interfaces*, 2018, **10**, 943.

- 45 C.-C. Chen, L. Dou, J. Gao, W.-H. Chang, G. Li and Y. Yang, *Energy Environ. Sci.*, 2013, **6**, 2714.
- 46 Y. Song, S. Chang, S. Gradecak and J. Kong, *Adv. Energy Mater.*, 2016, **6**, 1600847.
- 47 A. R. b. M. Yusoff, S. J. Lee, F. K. Shneider, W. J. da Silva and J. Jang, *Adv. Energy Mater.*, 2014, **4**, 1301989.
- 48 S. Berny, N. Blouin, A. Distler, H.-J. Egelhaaf, M. Krompiec, A. Lohr, O. R. Lozman, G. E. Morse, L. Nanson, A. Pron, T. Sauermann, N. Seidler, S. Tierney, P. Tiwana, M. Wagner and H. Wilson, *Adv. Sci.*, 2016, **3**, 1500342.
- 49 Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679.
- 50 W. J. E. Beek, M. M. Wienk, M. Kemerink, X. Yang and R. A. J. Janssen, *J. Phys. Chem. B*, 2005, **109**, 9505.