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Fully printed organic tandem solar cells using solution-processed silver nanowires and opaque silver as charge collecting electrodes†

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We report in this work efficient, fully printed tandem organic solar cells (OSCs) using solution-processed silver as the reflective bottom electrode and silver nanowires as the transparent top electrode. Employing two different band-gap photoactive materials with complementary absorption, the tandem OSCs are fully printed under ambient conditions without the use of indium tin oxide and vacuum-based deposition. The fully printed tandem devices achieve power conversion efficiencies of 5.81% (on glass) and 4.85% (on flexible substrate) without open circuit voltage (V_{oc}) losses. These results represent an important progress towards the realization of low-cost tandem OSCs by demonstrating the possibility of printing efficient organic tandem devices under ambient conditions onto production relevant carrier substrates.

Organic photovoltaics (OPV) have undergone rapid development in the last decade.^{1–4} Power conversion efficiencies (PCEs) of ~10% were reported for lab-scale single-junction organic solar cells (OSCs), owing to the emergence of novel high-performance donor materials as well as various device optimization methods.^{5–8} Along with these achievements, however, less attention has been paid to the development of fully printed devices despite

Broader context

One major benefit of organic photovoltaics (OPV) over their inorganic counterparts is that they can be solution-processed onto flexible substrates using high-throughput printing techniques. Thus, to fully exploit the cost potential of the OPV technology, printing the entire device stack under ambient conditions is highly demanded. However, the state-of-the-art high performance organic solar cells (OSCs) predominantly use sputtered indium tin oxide (ITO) as a transparent window electrode together with thermally evaporated metal (Ag, Al and Au) as a reflective counter electrode. The expensive raw material (indium) along with the costly fabrication procedure based on vacuum processing inevitably raises the final cost of OPV products to a level where they can no longer compete with alternative technologies. Although several solution-processed alternative materials have been discussed previously, none of these electrodes have achieved cell performances comparable with the ITO-metal based reference devices. Here, we identify two printed electrodes, silver nanowires and chemically converted silver, as an ideal electrode combination for construction of fully-printed single-junction as well as tandem OSCs. The outstanding optoelectronic properties of the two electrodes allow the resulting devices to exhibit negligible performance losses compared to their ITO-metal based reference cells.

their importance in lowering the production cost and eventually commercial applications. It is widely acknowledged that, in order to push the OPV technology towards practical applications, three essential requirements have to be fulfilled: high efficiency, long-term environmental stability and low-cost production.⁹

The efficiencies of single-junction OSCs are fundamentally limited by the narrow absorption bands and low carrier mobility of organic semiconductors. Stacking multiple light absorbers with different band-gaps to construct tandem devices offers the most effective way to boost the overall efficiencies of OPV devices.^{10–13} Theoretical calculations indicate that double-junction tandem OSCs hold the potential to reach PCE of >20%, showing an improvement of ~40% compared to the optimized single cells.^{14,15} Benefitting from recently developed efficient charge recombination layers and high-performance low band-gap materials, several research groups have reported tandem OSCs with PCEs of over 10%, which is considered to be the benchmark for practical applications.^{16–19}

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In order to compete with other photovoltaic technologies OSCs need to be processed by cost-efficient printing techniques which is a key requirement for rapid energy payback time.^{9,20–22} However, the overwhelming majority of efficient OSCs were fabricated in an inert atmosphere based on non-solution processed electrodes, such as sputtered indium tin oxide (ITO) and vacuum-deposited metals, which are energy and time consuming processes and inevitably increase the production cost.^{23,24} Therefore, the record performances of OSCs reported to date are impressive but do not directly contribute to the commercialization of the OPV technology.

In this regard, to make OPV technology industrially viable further cost reduction by fully printing the entire device stack under ambient conditions is highly demanded. However, due to the lack of high-performance solution-processable electrodes as well as the involved poorly-functioning interface layers, previously reported printed OSCs routinely showed fairly low performances compared to the reference cells based on ITO and vacuum deposited metal films.^{25–27} The low reflectivity of the counter electrodes led to insufficient absorption of incident light and thus photocurrent losses. In addition, the high roughness of the bottom electrodes together with the undesired interfaces generally resulted in large fill factor (FF) losses. In particular, when it comes to tandem configurations where the number of layers in the stack is almost twice that of single-junction counterparts, rational selection of electrode materials in combination with proper interface engineering becomes essential. Recently, some pioneering studies on fully printed tandem OSCs were reported by Krebs' group, demonstrating the possibility of continuous roll-to-roll printing of the entire tandem OPV devices. However, the obtained tandem devices showed rather low PCEs of <3%.^{28–31} It is apparent that these fully printed tandem devices suffered from significant losses in FF and open circuit voltage (V_{oc}).

In this work, through rational material selection we report ITO-free and fully printed tandem OSCs on both glass and polyethylene terephthalate (PET) substrates. Printed Ag converted from precursor ink and solution-processed silver nanowires (AgNWs) are employed as the bottom opaque electrode and the top transparent electrode, respectively. The outstanding optoelectronic properties of the two electrodes ensure sufficient light absorption in the active layers and efficient charge carrier collection. In combination with proper interface engineering, the resulting fully printed tandem OSCs without the use of ITO and vacuum-deposition steps achieve high PCEs of 5.81% and 4.85% on glass and flexible PET substrates, respectively.

To underline the significance of this work, it is necessary to have an overview of the past achievements in the development of fully solution-processed OSCs. Fig. 1 summarizes the PCE evolution of fully printed OPV devices in the past several years (see Table S1, ESI† for details). It is apparent that there is a steady improvement in the overall cell performance, reflecting the overall efficiency progress of the OPV technology, but the performance gap between record efficiency OSCs and fully printed OSCs is still large. As discussed above, these inferior performances of the fully printed devices are mainly due to the

Fig. 1 Efficiency evolution of fully printed organic solar cells. Details are summarized in ESI,† Table S1.

lack of high quality solution-processable electrodes as well as the undesired interface design. Both of the deficiencies will be addressed in the current work, not only for single-junction, but also especially for tandem OSCs.

Results and discussion

Currently, ITO is the most commonly-used electrode in various optoelectronic devices owing to its low sheet resistance and high optical transparency. However, the expensive fabrication technique based on vacuum-sputtering together with its brittle nature has hindered its application for large scale roll-to-roll manufacturing. To realize the efficient fully printed OSCs, the solution-processed transparent electrode is supposed to exhibit comparable optoelectronic properties to the ITO. Solution-processed AgNWs have recently attracted substantial attention as a transparent electrode for various organic as well as inorganic photovoltaic devices.^{32–38} The outstanding optoelectronic properties and successful device demonstrations encourage us to further exploit the application of AgNWs as a window electrode for our tandem devices. As shown in Fig. 2a, ~100 nm-thick AgNW-coated glass exhibits a high average visible transmittance of 80%, which is comparable to the ITO-coated glass (81%). The reduced transmittance at wavelengths of around 380 nm is mainly due to the plasmonic absorption of AgNWs. Concerning electrical properties, the printed AgNW electrode shows a low sheet resistance of $\sim 10 \Omega \square^{-1}$, which is comparable or even superior to that of commercial ITO electrodes.

In order to maximize the photocurrent generation in the devices, the counter electrode should be highly reflective to allow for a second passage of photons through the active layer. Solution-processed opaque Ag films converted from precursor ink have recently drawn much attention because of their substantially reduced fabrication cost as compared to the vacuum processed counterparts.^{29,39} To prepare a Ag electrode from solution, an annealing step at 130 °C is carried out to convert the as-deposited Ag precursor film to a reflective Ag layer. It was observed that the as-prepared Ag film showed poor adhesion on the glass substrate owing to a high density of bubbles which

Fig. 2 (a) Optical properties of the printed AgNWs and Ag electrodes. (b) Digital photos of bare glass (upper-left) and AgNWs (upper-right), printed Ag (lower-left) as well as vacuum-evaporated Ag (lower-right) coated glasses. (c) AFM images of the printed AgNWs (left) and Ag electrodes (right) on glass.

formed during the conversion process (Fig. S1, ESI†). In order to get rid of this negative effect, prior to the Ag electrode deposition an additional poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) thin layer was printed onto glass, which effectively eliminated the formation of bubbles and thus greatly increased the adhesion between the printed Ag and the substrate. To evaluate the optical properties of the printed Ag electrode, the reflectivity of the film was measured and compared to that of a vacuum-deposited Ag film. As shown in Fig. 2a, the printed Ag exhibits an average reflectance as high as 98% in the range of 380–900 nm, almost identical to that of evaporated Ag. In addition, the printed Ag film with a thickness of about 200 nm shows a low sheet resistance of $1 \Omega \square^{-1}$ which is also as good as that of the evaporated Ag ($0.8 \Omega \square^{-1}$). Digital photos of bare glass, solution-processed AgNWs, printed Ag as well as vacuum-evaporated Ag covered glasses are displayed in Fig. 2b.

It should be noted that, in addition to decent optoelectronic properties, the involved bottom electrode should possess low surface roughness in order not to cause shunts in the devices and, more importantly, the integration of the top electrode should not compromise the device functionality. The surface roughness of the two printed films was thus investigated by atomic force microscopy (AFM) measurement. As shown in Fig. 2c, the printed Ag electrode exhibits a low surface roughness of 3.3 nm (root mean square-rms roughness), which is much lower than that of the AgNWs which is 13.4 nm. Although AgNW networks can be used as both the bottom and/or top electrodes for OSCs with proper surface modification, the converted Ag is expected to be more favorable as a bottom electrode for our fully printed tandem devices

due to its lower surface roughness, which is important for achieving favorable morphology of upper several layers and thereby preventing shunts in the devices.⁴⁰ In addition, we have observed that the opaque Ag electrode can completely short the devices when employed as the top electrode. We suspect that this negative effect is probably due to the fact that the Ag precursor ink can infiltrate into the underlying layers and present short-circuit paths after thermal conversion.

To evaluate the potential of the above proposed two solution-processed electrodes, fully printed single-junction devices were first designed and constructed step by step, replacing the two electrodes of a reference cell (device #1), vacuum-deposited Ag and sputtered-ITO, with printed AgNWs and Ag, respectively, as illustrated in Fig. 3a. It is worth mentioning that we have employed a normal architecture for all our devices, which allows us to replace the electron extraction layer, which is typically Ca, by solution-processed ZnO nanoparticles. More importantly, the introduced ZnO layer can effectively serve as a mechanical foundation enabling doctor blading of AgNWs from a water based solution. As a first step, the top evaporated Ag electrode of the reference cell was substituted by printed AgNWs, resulting in a semitransparent OSC (device #2). Successively, the bottom ITO of the semitransparent cell was replaced with printed Ag, giving a fully printed opaque single-junction OSC (device #3).

Fig. 3b shows the $J-V$ characteristics of the investigated single-junction OSCs, which were illuminated under simulated AM 1.5G spectrum with a light intensity of 100 mW cm^{-2} . Employing a low bandgap diketopyrrolopyrrole–quinoxaline alternating copolymer (pDPP5T-2),^{41,42} blended with PCBM as

Fig. 3 (a) Schematic illustration of development towards fully printed OSCs. Three different electrode combinations, ITO/vacuum-deposited Ag (#1), ITO/printed AgNWs (#2) and printed Ag/printed AgNWs (#3), were employed for different architectures to demonstrate the technique development. (b) J - V characteristics of the investigated single-junction OSCs incorporating different electrode combinations. (c) EQE characteristics of the corresponding single-junction OSCs.

the photoactive layer (chemical structures are shown in Fig. S2, ESI†), the reference cell device #1 showed a short circuit current density (J_{sc}) of 13.61 mA cm^{-2} , a V_{oc} of 0.56 V and a FF of 63%, yielding a PCE = 4.8%. Due to the absence of a back reflective electrode, the semi-transparent cell device #2 exhibited a lower J_{sc} of 8.54 mA cm^{-2} . Nevertheless, the fully printed OSC device #3 showed a J_{sc} of 13.39 mA cm^{-2} , a V_{oc} of 0.57 V and a PCE of 4.74%. All of these photovoltaic parameters are comparable to that of the control device #1, indicating the successful replacement of sputtered ITO and vacuum-deposited Ag with printed opaque Ag and AgNW electrodes for single-junction OSCs. External quantum efficiency (EQE) characteristics shown in Fig. 3c confirmed the respective photon-responses of the three investigated OSCs. Not surprisingly, one can see that the fully printed device with illumination from the top AgNWs side shows a minimum in photocurrent generation in the range of 350–450 nm, corresponding to the plasmonic absorption of the AgNWs.

The fully printed tandem OSCs were realized by introducing both printed electrodes into the tandem configuration. The device architecture of tandem OSCs is illustrated in Fig. 4a. Owing to their promising air-processing compatibility, two spectrally complementary polymer donors, GEN-2 and pDPP5T-2, which have been intensively studied previously, were employed as photoactive materials.^{11,14} The absorption spectra of the two

active layers (donor blended with acceptor PCBM) are shown in Fig. S2 (ESI†). The two sub-cells were effectively connected in series with a solution-processed intermediate layer (IML) consisting of ZnO and neutralized PEDOT:PSS (N-PEDOT).¹² A cross-sectional conventional transmission electron microscopy (CTEM) image of the tandem device clearly showing the position and thicknesses of all layers is given in Fig. 4b. High angle annular dark field (HAADF) image and elemental maps obtained using energy dispersive X-ray analysis (EDX) in scanning transmission electron microscopy (STEM) mode, showing the composition of the layers and the interfaces are given in Fig. 4c. As shown in Fig. 4b, all the printed layers can be clearly distinguished from the cross-section without any interlayer mixing. The distinct interface between the zinc and sulfur as revealed in EDX mapping (Fig. 4c) confirms that the bottom- and top-cells of the printed tandem device were physically separated by the solution-processed IML.

For reference purposes, tandem as well as the corresponding single-junction OSCs based on ITO-coated glass and vacuum-deposited Ag electrodes were constructed. The J - V characteristics of the prepared reference devices are summarized in Fig. 4d and Table 1. The optimized reference tandem cells based on ITO-coated glass and vacuum-deposition Ag electrodes gave high PCEs of $\sim 6.5\%$. Then, the fully printed tandem OSCs were successfully realized on glass by combining the printed Ag and AgNWs with

Fig. 4 (a) Schematic illustration of the device structure of fully printed organic tandem solar cells. (b) Cross-sectional conventional transmission electron microscopy (CTEM) image clearly evidences all the component layers without layer damage and interlayer mixing. Note that the specimen used for CTEM characterization had the active layers' thicknesses not corresponding to the optimized thicknesses of our champion devices. (c) Scanning transmission electron microscopy (STEM) image with EDX maps showing elemental chemical analysis of a fully printed tandem OSC on glass. To have a better visual perspective, the maps for Ag and S have been changed as to heighten the signal of AgNWs and lower the signal of sulphur. (d) J - V characteristics of the single-junction as well as tandem reference devices. (e) J - V characteristics of the fully printed tandem OSCs on glass and on PET. The reference tandem cell #5 (dashed gray line) is added for comparison.

Table 1 Photovoltaic parameters of the investigated single-junction and tandem OSCs

Device	Architecture	V_{oc} [V]	FF [%]	J_{sc} [mA cm ⁻²]	PCE [%]	R_p^b [kΩ cm ²]	R_s^b [Ω cm ²]
#1	Glass/ITO/pDPP5T-2/Ag	0.56	63	13.61 ^a	4.80 (4.73)	16.2	2.4
#2	Glass/ITO/pDPP5T-2/AgNWs	0.57	61	8.54 ^a	2.97 (2.87)	27.5	3.5
#3	Glass/P_Ag/pDPP5T-2/AgNWs	0.57	62	13.39 ^a	4.74 (4.58)	26.6	3.9
#4	Glass/ITO/GEN-2/Ag	0.75	64	11.0 ^a	5.28 (5.20)	192.6	1.3
#5	Glass/ITO/GEN-2/pDPP5T-2/Ag	1.29	66	7.61	6.48 (6.28)	401.2	14.3
#6	Glass/P_Ag/GEN-2/pDPP5T-2/AgNWs	1.29	61	7.38	5.81 (5.62)	26.3	17.0
#7	PET/P_Ag/GEN-2/pDPP5T-2/AgNWs	1.28	54	7.02	4.85 (4.58)	46.5	25.4

^a J_{sc} values were calculated by integrating EQE spectra with the standard solar spectrum AM 1.5G. ^b Parallel resistance (R_p) and series resistance (R_s) were calculated at around 0 V and 2 V, respectively. Note: the PCE results listed in the brackets are the average values based on around 30 measured devices.

optimized semiconducting components. The photocurrents generated within the tandem device were experimentally matched by keeping the bottom active layer with a thickness of ~ 200 nm, which is optimized for the GEN-2:PCBM single-cell, and fine tuning the thickness of the top active layer (front cell, in this case) in the range of 80–100 nm. More than 30 tandem

devices were constructed and the champion tandem cell exhibited a V_{oc} of 1.29 V, along with a J_{sc} of 7.38 mA cm⁻² and a FF of 61%, resulting in a high PCE of 5.81%.

In order to better analyze the current generation within the two sub-cells, electric field intensity and absorption density distributions in the entire device stack were examined. As shown

in Fig. S3 (ESI[†]), the thicknesses of the two active layers critically influence the overall absorption of the active layers. Due to the fact that the low band-gap polymer pDPP5T-2 possesses a higher absorption coefficient than the GEN-2, a balanced absorption density can be achieved when the thicknesses of the front pDPP5T-2:PCBM and back GEN-2:PCBM sub-cells are fixed to 80 and 200 nm, respectively. For a thickness combination of 30/250 nm, the current generation in the pDPP5T-2 layer cannot match the current generation in the GEN-2 layer, whereas it is the other way around for a thickness combination of 200/80 nm. To obtain an overview of the potential performance of our tandem devices, the overall PCE as a function of the thicknesses of the two active layers was also plotted. As shown in Fig. S4 (ESI[†]), the measured PCE of 5.81% is in good agreement with the outcome of simulations. EQE characterizations of the printed tandem cells under blue and infrared light bias were further carried out (Fig. S5, ESI[†]), which confirmed the accuracy of our J - V measurement.

It is well known that a polymer binder, *i.e.* polyvinylpyrrolidone (PVP), is commonly used to synthesize and environmentally stabilize AgNWs and further form the matrix of the AgNW film.^{43,44} The matrix formed by the protective polymer binder prevents the metallic individual AgNWs from directly contacting the underlying ZnO nanoparticles. As evidenced in Fig. S6 (ESI[†]), thin amorphous regions between ZnO and AgNWs are probably the origin of the increased series resistance (R_s) and thus contributed to the relatively low FF of the fully printed tandem devices compared to the reference tandem cell (61% *vs.* 66%). The thermal stability as well as stability under continuous UV light illumination of the fully printed tandem OSCs was investigated and the results are presented in Fig. S7a and S7b (ESI[†]). The fully printed tandem devices show excellent stability at 100 °C, while the performance decreases dramatically upon increasing the baking temperature up to 140 °C.

To demonstrate the general applicability of the printing technique to different carrier substrates, PET was employed to replace the rigid glass substrate for the fully printed flexible tandem OSCs. Printed Ag on PET (Fig. S8a, ESI[†]) exhibits a sheet resistance of $\sim 1.2 \Omega \square^{-1}$, which is comparable to that on glass. However, the rms roughness of the printed Ag on PET was determined to be 6.34 nm (Fig. S8b, ESI[†]), which is about 2 times higher than that of the printed Ag on glass. This high rms roughness of the printed Ag on PET may be attributed to the combination of the original roughness of PET and the deformation of PET during the conversion of the Ag precursor at 130 °C. Although the high roughness does not influence the sheet resistance of the Ag electrode, it may cause shunts as well as increase the R_s of the entire device owing to the unfavorable contact between the electrode and the interfacial layer. Nevertheless, a PCE of 4.85% along with a V_{oc} of 1.28 V and a J_{sc} of 7.02 mA cm^{-2} were achieved for the fully printed tandem OSC on PET. The J - V characteristics of the fully printed tandem devices on glass and on PET are summarized in Fig. 4e and Table 1. Compared to the fully printed tandem OSC on glass, the slightly reduced PCE of the flexible device is mainly due to the relatively low FF of 54%, which can be ascribed to its high

R_s of $25.4 \Omega \text{ cm}^2$. Because all the semiconducting layers and electrodes were printed under the same conditions as device #6, we ascribe the increased R_s of the flexible tandem devices to the high roughness of the bottom Ag electrode as well as the unfavorable interfaces between electrodes and semiconducting layers due to the deformation of the PET substrate during device fabrication, *e.g.* thermal-annealing process.

Compared to those results reported in the literature, the performance of our fully printed tandem OSCs on a flexible substrate was significantly improved to approach 5%. Remarkably, both of our fully printed devices on glass and PET substrates showed no significant photocurrent losses compared to reference cells. However, owing to the relatively increased series resistance, a PCE reduction of $\sim 10\%$ was observed by introducing two solution-processed electrodes for fully printed tandem devices, and a further PCE loss of $\sim 15\%$ was observed when processed on a flexible substrate. We believe these performance losses can be partially recovered by employing the binder-free AgNWs to increase the ohmic contact between the nanowires and underlying interface layer. In addition, thermal-stable flexible substrates with low roughness and the use of a novel reflective electrode that can be processed at low temperatures will ultimately eliminate negative effects on the FF losses.

To conclude, we demonstrated fully printed tandem OSCs on glass and PET substrates by introducing a solution-processed highly reflective Ag layer and transparent AgNWs as charge collecting electrodes. The contact properties at the interfaces between printed Ag and glass as well as between ZnO and AgNWs were studied by means of cross-sectional TEM imaging. PCEs of 5.81% and 4.85% were achieved for our fully printed tandem solar cells prepared on glass and PET substrates, respectively, which are, to the best of our knowledge, the highest efficiencies for fully printed tandem OSCs. Our work demonstrates an important progress towards realization of the cost potential of fully printed tandem OSCs, and also the possibility of environmentally printing tandem OSCs onto production relevant carrier substrates with promising performances.

Experimental

Materials

Light absorbers pDPP5T-2 (batch: GKS1-001, $M_w = 47\,000 \text{ g mol}^{-1}$, PDI = 2.2) and GEN-2 were received from BASF and Merck, respectively. PEDOT:PSS (Clevios[™], P VP AI 4083) and neutral PEDOT:PSS (NT5-3417286/2) were purchased from Heraeus and Agfa, respectively. ZnO nanoparticles dispersed in isopropanol (Product N-10) were supplied by Nanograde AG. PCBM (99.5%) was purchased from Solenne BV. Silver ink (TEC-PR-010) and AgNWs dispersion (ClearOhm ink) were received from InkTec and Cambrios Technologies Corporation, respectively. All the materials were used as received without further purification.

Fabrication of tandem OSCs

For fully printed tandem solar cells, all the layers were deposited on either glass or PET substrates using doctor blading in an ambient atmosphere. The substrates were cleaned by ultra-sonication in

acetone and isopropanol for 10 minutes each. Prior to the deposition of the Ag electrode, PEDOT:PSS (1:3 vol% diluted in isopropanol) with a thickness of ~ 20 nm was doctor-bladed onto substrates to enhance the adhesion between the substrate and the Ag electrode. Ag ink was then doctor-bladed at 50°C from its original solution and baked at 130°C for 5 min to obtain the reflective Ag bottom electrode with a thickness of ~ 200 nm. Successively, ~ 40 nm-thick PEDOT:PSS as a electron-blocking layer was deposited on the opaque Ag bottom electrode and dried at 130°C for 5 min. GEN-2:PCBM (1:2 wt%), dissolved in dichlorobenzene at a total concentration of 30 mg mL^{-1} , was bladed to form the first active layer with a thickness of ~ 200 nm. Afterwards, a charge carrier recombination layer consisting of ZnO nanoparticles and neutral PEDOT:PSS was subsequently deposited on top of the first active layer from their original solution and dried at 80°C for 3 min each. The second active layer, pDPP5T-2:PCBM (1:2 wt%), was coated from a mixed solvent of dichlorobenzene:chloroform (1:9 vol%) at a total concentration of 24 mg mL^{-1} . The ZnO nanoparticles were then deposited again on top of the second active layer to serve as an electron transporting layer and dried at 80°C for 5 min. The whole stack was finalized by doctor-blading AgNWs with a thickness of ~ 100 nm to form the transparent top electrode.

All reference cells in a normal architecture were processed in a similar approach as the fully printed tandem cell. The top electrode consisting of Ca/Ag (15/100 nm) was thermally deposited under a vacuum of 10^{-6} torr.

Characterization

All the J - V characteristics were recorded using a source measurement unit from BoTest. Illumination was provided by a solar simulator (Oriel Sol 1A, from Newport) with AM 1.5G spectra at 100 mW cm^{-2} , which was calibrated by a certified silicon solar cell. The active area of the constructed OSCs was defined by the overlap of the bottom and top electrode, which was determined to be 10.4 mm^2 for the OSCs based on ITO-coated glass and vacuum-deposited Ag electrodes and $\sim 15\text{ mm}^2$ for the fully printed OSCs. The optical and morphological properties of the electrodes were investigated using a UV-Vis-NIR spectrometer (Lambda 950, from Perkin Elmer) and an atomic force microscope (Veeco Model D3100, tapping mode). The thicknesses of the films were measured using a profilometer (Tencor Alpha Step D 100). The EQE spectra were recorded using an Enli Technology (Taiwan) EQE measurement system (QE-R), and the light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The liftout sample for TEM was prepared with FEI Helios Nanolab 660 DualBeam FIB, from the area of interest containing all layers of the solar cell, with a carbon protective deposit to avoid amorphization of Ag nanowires, if directly struck by the Ga ion beam. A lamella containing a cross section of the solar cell was then attached to a TEM half grid for final thinning. The final thickness of the liftout sample was kept below 100 nm, in order to enable high quality CTEM imaging at an acceleration voltage of 200 kV. Transmission electron microscopy was performed on

the FEI TITAN³ Themis 60–300 double aberration corrected microscope at the Center for Nanoanalysis and Electron Microscopy (CENEM), University of Erlangen, equipped with the super-X energy dispersive spectrometer.

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