Highly Reflective and Low Resistive Top Electrode for Organic Solar Cells and Modules by Low Temperature Silver Nanoparticle Ink

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One of the issues that have caused a wide performance gap between commercially available organic photovoltaic (OPV) modules and the hero cells in literature lies in the lack of printable and roll-to-roll process compatible high-performance top electrodes. This work takes an unorthodox approach to this issue by developing a printable silver nanoparticle (AgNP) film top electrode that can achieve a similar performance as evaporated ones (EvapAg). It illustrates the developmental process from ink formulation to the critical processing conditions that are tailored for OPV devices procedurally. The resultant cells and modules with AgNP electrodes have achieved almost the same power conversion efficiencies (~90%) as those with evaporated silver electrodes, as demonstrated for multiple material systems, printing methods, as well as layouts. Under low light condition, AgNP cells perform even significantly better than EvapAg ones, due to their lower leakage currents. More importantly, this work has demonstrated that fully printed OPV modules can achieve similar performance as small scale OPV cells with evaporated electrodes when both the electrical and optical performance of their top electrodes are comparable. With the latest generation of materials, this approach offers an attractive alternative for manufacturing of highly efficient OPV modules at large scale.

1. Introduction

The efficiency of solution processed industrially produced OPV modules has continuously increased from about 2% in 2007[1,2] to about 5% in 2016, with some notable exceptions for prototype modules up to 12%. [3–7] While there has been a major breakthrough in power conversion efficiency (PCE) for organic photovoltaic (OPV) in recent years, the top electrodes among these device structures are exclusively EvapAg. Their typical device structure and their respective processing method are summarized in Figure 1a. These device structures are highly unfavorable for production, considering the setup and operating cost of operating both solution and vacuum deposition process in a single production line. On the contrary, many mass produced OPV modules are solution processed.[8,9] Their top electrodes are usually a combination of resistive but semitransparent PEDOT:PSS (hc-PEDOT) layer and a screen-printed highly conductive opaque silver grid.[10,11] This kind of meshed grid electrodes make the device semitransparent, which is one of the major advantages of OPV over other contemporary photovoltaic technologies. The typical cell structure and processing method of manufactured OPV modules is summarized in Figure 1b.

While these types of composite top electrodes are widely established in production environments, they are unavoidably a compromise between minimizing the sheet resistance and the optical disturbance introduced by the opaque silver grid. As state-of-the-art devices with higher short circuit current ($I_{sc}$) are becoming available, the grid coverage has to be increased dramatically in order to minimize the electrical resistance, which further impedes the optical homogeneity of the devices.[12] Most importantly, the lack of a reflective electrode incurs significant losses to $I_{sc}$ as the single pass photoabsorbance of the photoactive layer (PAL) of these record efficiency cells is relatively low.[13–15] These losses, when added with the electrical losses, will...
unavoidably widen the performance gap between reported hero cells and the mass produced OPV modules. There are already a lot of studies on printable top electrodes to replace the current composite top electrode in literature. Many publications focus on balancing the transmittance of the device versus its overall efficiency, which is often limited by the PAL thickness and the top electrode sheet resistance. There are also a few works that use low melting point eutectic metal alloys as top electrodes, but the results are quite limited.

This highlights one of the issues in printed OPV: the lack of higher performance alternatives to the transparent electrodes. As a result, currently there are only semitransparent printed OPV modules on the market. While semitransparency is one of the major advantages for OPV, it should not be the only type of device that is available. In many applications, e.g., in nontransparent parts of facades, a higher performance alternative is needed.

On the other hand, printed silver films do exist and are widely used in printed electronics. The AgNP films often exhibit excellent conductivity and are widely used to produce highly conductive circuit tracks by additive manufacturing methods. There are also works that have fabricated current collecting grids for bottom electrodes in organic electronic devices. However, most AgNP inks are designed specifically for electronics applications and their formulation often contains additives and solvents that are incompatible with the processing requirements of the stacked layer structure in OPV devices. This often results in dissolution of the hole extraction layer (HEL) and even other layers further down in the stack. An example of such occurrence is shown in Figure 1d where the AgNP ink used to print the top grid electrode has mixed with the layers underneath. This challenge is exacerbated as the amount of ink increases when printed area increases or the printing method requires it. Furthermore, many ink formulations require sintering temperatures above 140 °C in order to achieve good electrical conductivity, meaning that the whole stack has to withstand this temperature, because otherwise degradation of performance would be observed for typical OPV devices. Thus, OPV cells and modules with printed top grid electrodes are often very limited due to the large series resistance introduced by the
electrode. Furthermore, the reflectance of these AgNP films reaches at best only 55% at visible wavelengths, which is far lower than the values of their evaporated counterparts. Figure 1e compares the reflectance spectra between EvapAg and AgNP films printed from a commercial formulation. This gap in reflectance significantly reduces the short circuit current density ($J_{sc}$) that can be achieved and hence diminishes the merit of printed AgNP films as top electrode. Few works that have made such attempts have achieved only relatively mediocre results with around 20% loss in PCE compared with reference devices with evaporated electrodes.[32,33] Han et al. circumvented these issues by depositing UV sinterable silver paste as top electrode, in which the UV sensitive photoactive layer is protected by a bilayer HEL to prevent photo-oxidation during the photosintering process.[34] While this work has presented a novel approach in adapting silver inks for organic solar cell fabrication, the performance gap between the hero cells and printed modules remains large, likely due to the large series resistance of the UV sintered silver top electrode.

To minimize the performance gap between partially solution processed research cells in literature and printed but mediocre production modules, better AgNP electrodes that are specifically tailored for scalable OPV fabrication need to be developed. First, in order to address all the aforementioned issues with AgNP inks and their processing, new ink formulations are tailored specifically for various OPV printing methods. Based on a low sintering temperature, AgNP paste that has only a minimal amount of additives, the dispersion solvent is analyzed for the best stability and weakest solubility against organic layers. The printing and annealing processes are also optimized systematically in order to achieve electrical and optical properties comparable to EvapAg films while being compatible to OPV fabrication. The AgNP electrodes are then printed on OPV cells with various fullerene and nonfullerene-based PALs and compared with reference cells with EvapAg electrodes. The results showcase that printed OPV cells with architectures similar to those used in mass production (Figure 1b vs Figure 1c) can indeed achieve similar levels of efficiency as research cells with EvapAg electrodes when their top electrode characteristics are comparable. Finally, a series of monolithic printed OPV modules with AgNP top electrodes are fabricated to show that compatibility with modularization processes, such as LASER patterning can be achieved without substantial process adjustment, paving the way toward higher geometric fill factor (GFF) devices. More importantly, this work demonstrates experimentally that the performance gap between cells and modules can be largely negated by high performance top electrode and previously discussed rational module layout,[35,36] thus achieving the highest efficiency in ITO based, vacuum free printed organic solar modules.[22]

2. Results and Discussion

2.1. AgNP Ink Formulation for OPV

2.1.1. Solvent Choice for AgNP Dispersion

A special low sintering temperature AgNP paste, DF-AT-2011 was supplied by DOWA Electronics Materials for this work. The paste contains 88.8 wt% silver and additional 8.7 wt% of diethylene glycol butyl ether (DGBE) with the remaining components being surfactant and dispersant. The paste is diluted to 20 wt% silver with various solvents by ultrasonication and planetary centrifugal mixers. Solvents which redissolve Polystyrene sulfonate in the PEDOT:PSS layer cannot be used if changes to the HEL work function are to be avoided. Ideally, the solvent should also be orthogonal to the donor:acceptor layer underneath the HEL. However, most solvents that can form a stable AgNP dispersion (at least 1 week in ambient after dilution, see Supporting Information for explanation) are nonpolar and hence show good solubility with common nonfullerene acceptors (NFAs), such as o-IDTBR. This study focuses on the solubility with acceptor as it is a small molecule, which exhibit much better solubility than the polymer donor. The results are summarized in Table 1. From these results, it is clear that ethylene glycol offers the best ink stability. Among them, ethylene glycol butyl ether is chosen as the solvent due to its optimal drying temperature for both inkjet and doctor blade coating at 65°C.[37] In order to prevent solvent diffusion into the PAL, the PEDOT:PSS layer has to be cross-linked, which is often done to prevent dissolution of underlying layers in a stacked structure.[38,39]

2.1.2. Investigation of AgNP Properties

The median particle size for the AgNP paste is specified as 90 nm by the manufacturer. However, SEM images taken on a coated but nonsintered sample show a significant discrepancy from this value (Figure 2a). The calculated particle size distribution shown in Figure 2b indicates that the median particle size is around 50 nm for a sample size of 310 particles. Furthermore, larger clumps formed by smaller AgNPs are also observed occasionally.

2.2. AgNP Film Properties

It is commonly known that the sintering conditions have a significant impact on the electrical resistivity of the sintered AgNP film. Higher sintering temperature and longer sintering time promote the densification of the film and thus lead to properties closer to bulk silver resistivity.[40,41] However, in order to utilize AgNP as printable top electrodes, the film must be able to reach a

| Solvent                | Solvent coloring | Film dissolution | Sedimentation |
|------------------------|------------------|------------------|---------------|
| Toluene                | Very strong      | Yes              | >1 week       |
| Anisole                | Strong           | Yes              | <1 week       |
| 1,2-Dichlorobenzene    | Very strong      | Yes              | <1 week       |
| DGBE                   | Strong           | Yes              | >1 week       |
| 1-Octanol              | Medium           | Yes              | <1 week       |
| Ethylene glycol ethyl ether | Weak          | Yes              | <1 week       |
| Ethylene glycol propyl ether | Medium   | Yes              | >1 week       |
| Ethylene glycol butyl ether | Medium  | Yes              | >1 week       |
| Iso-propanol           | No               | No               | <1 week       |

Table 1. Solubility of P3HT:o-IDTBR film by target solvent. One week after dilution of AgNP paste, the ink is tested for signs of sedimentation after being stored in a cabinet in the ambient. Figure S1, Supporting Information, shows the color and film changes after testing.
reasonable sheet resistance at relatively low sintering temperature within relatively short time before the cell stack, in particular the PAL, becomes denatured. This implies that most of the additives should be reacted after annealing so that the contact resistance between AgNP layer and HEL is minimal. Common annealing conditions for OPV materials are usually up to 140 °C for 5 min. Thus, the properties of AgNP films sintered at similar conditions are investigated, i.e., at 120, 140, and 160 °C for 5 min. Table 2 lists the sheet resistance, thickness, and resistivity of the AgNP films sintered at these temperatures while their respective SEM images are shown in Table 3. Compared to Figure 2a, it is clear that individual AgNPs are fused together to form a percolating conductive film when heated at an elevated temperature for a short time, as also demonstrated by other works. The fusion between individual AgNPs is increased with temperature, which in turn lowers the sheet resistance and resistivity of the films tested. Several works have provided an excellent insight on the sintering mechanisms of AgNP in this regard. The resistivities of the AgNP films are generally higher for thicker films even at the same sintering condition. This is also reflected in the SEM images where the connections between patches of “AgNP islands” are less pronounced compared with thinner films. Overall, most samples (except those sintered at 120 °C) exhibit a resistivity of less than 10 μΩ cm and under the best condition, having thus reached 40% of bulk silver conductivity, thanks to the extensive sintering in most AgNP films. However, Table 2 also shows that the sheet resistances of most samples are well below 1 Ω cm−1 and thus will not be the dominating factor for the overall series resistance of the cells or modules. Thus, the optical reflectance, which directly affects \( J_{sc} \) of the device fabricated, is the critical process optimization parameter.

While there are a lot of investigations on the electrical properties of printed AgNP films, their optical properties are not very well studied. It is clear that the size of metallic particles will have a significant impact on the surface plasmonic resonance peak position and its intensity. As a result, AgNP films that are better sintered, and hence better fused should also exhibit higher total reflectance and lower film absorbance in general. The results from the previous two tables have also reverberated on the reflectance spectra in Figure 3a where samples with lower sintering temperature and higher film thickness also have weaker reflectivity. Since all the samples have very similar transmittance curves (Figure 3b), films that are sintered at lower temperature or have higher thickness apparently have higher absorbance than those sintered at higher temperature or have lower film thickness. Overall, most AgNP films exhibit reflectance values of over 70% in the spectral range of interest for OPV materials (400–850 nm), which is ≈20% higher than its commercial counterparts but is still ≈20% lower than those of EvapAg films.

It is clear from the result that a sintering temperature below 120 °C is rather unsatisfactory while 160 °C is too high for OPV fabrication, particularly for flexible substrates. Thus, the maximum temperature used in this work is limited to 140 °C for 5 min, which is the process limit for PET substrates.

### 2.3. AgNP Top Electrode for OPV

To ensure process compatibility of the additional printing and sintering step, AgNP films are printed as top electrodes for

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**Table 2.** Sheet resistance, film thickness, and resistivity of AgNP films thermally sintered at various temperatures for 5 min and coated with different doctor blade speeds.

|            | 120 °C Ω cm−1 | 140 °C Ω cm−1 | 160 °C Ω cm−1 |
|------------|---------------|---------------|---------------|
| SR [Ω cm−1] | T [nm]        | \( \rho [\mu\Omega \text{cm}] \) | \( \rho [\mu\Omega \text{cm}] \) |
| 5 mm s     | 5.6           | 142           | 79.4          |
| 10 mm s    | 2.05          | 207           | 42.4          |
| 20 mm s    | 0.95          | 323           | 30.7          |

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OPV cells (0.1 cm²). Three types of donor/acceptor combinations are tested, which are P3HT:o-IDTBR, PV2000:PCBM, and PM6:Y6. Full area electrodes that are equivalent to the evaporated electrodes reported in literature are coated by doctor blade, as are the other printed layers in the device structure. On the other hand, grid electrodes that are commonly used in device layouts in commercial OPV modules are mimicked by inkjet printing in this work. These two methods are selected for top electrode deposition as inkjet printing offers the freedom of shapes while doctor blade coating is much closer to slot die coating in production environments. Similar to the standard manufacturing procedure for OPV modules, an additional LASER patterning step is required to define the device area for all doctor blade coated devices.

The performance data of PV2000:PCBM cells with full area Ag top electrodes are shown in Figure 4. The PV2000:PCBM represents one of the most common state-of-the-art materials used in mass production of OPV modules. Up to 8% PCE with EvapAg was demonstrated by the manufacturer in a publication by vacuum and solution processing. In this work, the PCE that is obtained with a similar device structure but with a cross-linked PEDOT:PSS layer underneath the electrode and fabricated in ambient environment is around 7.3% at 1000 W m⁻² illumination (solid line black boxes). With doctor blade coated full area AgNP electrodes an efficiency as high as 6.9% (solid line green boxes) is achieved, with mean PCE at around 6.5% (red, green, blue, and cyan boxes), which is around 5% difference when compared with EvapAg. In comparison, other works with printed transparent silver nanowire electrodes with the same device structure and material system have only reported an efficiency 4.3% at best. By forgoing semitransparency, this work has demonstrated experimentally that the performance loss incurred by printing an additional electrode layer deposition can be negligible when the ink and its treatment process are properly designed.

The major loss in PCE with AgNP electrode can be attributed to the lower J_sc, which in turn is attributed to the weaker reflectance of printed AgNP electrodes (Figure 3a). The mean J_sc for cells with EvapAg and AgNP top electrodes (except 320 nm) are around 14.3 and 13.5 mA cm⁻² respectively, which is around 5% difference. On the other hand, the external quantum efficiency (EQE) calibrated J_sc values in Figure S4, Supporting Information, show a difference in J_sc of around 9%. The IPCE spectrum have also indicated a wider EQE gap at shorter wavelengths (<600 nm) between the two types of devices when compared with longer wavelengths. This is due to the weaker reflectance of AgNP films when compared with EvapAg films at these wavelengths (see Figure 3a). This results in weaker absorption and hence
lower photocurrent generated. All other performance parameters, i.e., Voc, FF are almost the same compared with devices with EvapAg electrodes. As a result, the current voltage characteristics in Figure 4g,h are almost identical with different top electrodes. It is only at high forward applied bias that the difference in current injected through the cells starts to become visible.

It should also be noted that the leakage currents for cells with AgNP films are much lower than for cells with EvapAg films, which is critical in low light energy harvesting. This is due to the lack of thermal diffusion and deposition damages incurred during thermal evaporation of silver. To demonstrate how this parameter can affect the cell performance, some of the best performing devices (EvapAg and 140 nm AgNP) are measured again at 16 W m⁻² under the same illumination spectrum, which very roughly translates to the illumination inside an electronic workshop. The results are presented on the right side of Figure 4a–e using boxes with dashed lines. The loss in Voc and FF for cells with EvapAg electrodes are clearly visible as the light intensity is reduced. This is in general agreement with our theoretical study on the characteristics of solar cells under low light condition. Besides, the Jsc of cells with EvapAg electrode are also significantly lower than their AgNP counterparts. Extrapolating the average current densities at 1000 to 16 W m⁻² results in 0.23 and 0.22 mA cm⁻² for cells with EvapAg and AgNP electrodes, respectively. However, actual measurement indicates that the Jsc for cells with EvapAg electrodes (0.16 mA cm⁻²) have dropped by more than 30% while the cells with AgNP electrode (0.25 mA cm⁻²) have roughly agreed with the calculation. This is attributed to the different ratios of leakage current to photocurrent generated under such illumination condition. At such low light intensity, the photocurrent generated is only about 30 μA for the cell size used, which is in the same order of magnitude as the leakage current of cells with EvapAg electrode. The median leakage current for cells with EvapAg electrode is 23 μA, while it is around 1 μA for cells with AgNP electrodes. Overall, cells with EvapAg electrode have lost more than half of their efficiency while cells with AgNP electrode can still maintain the 6.5% PCE when measured at 16 W m⁻². This has clearly showcased the advantage of AgNP electrode over its evaporated counterpart. This attribute is very useful for power generation under low light condition, such as indoor energy harvesting for internet of things.

As a side note, some other works have demonstrated an increase in PCE when their cells are measured with an indoor lighting source, which contradicts with the findings in this work. This is due to the difference in spectral matching between the absorption spectrum of the cell and the illumination spectrum of the light source as this work measures the low light performance data using the attenuated standard solar spectrum. Thus, it is also reasonable to expect that the actual PCE should be even higher when the cells with AgNP electrodes are measured using fluorescent lamps as in some of these works.

While PV2000:PCBM is commonly used in production, NFA PALs have shown much promises lately. Two PALs containing NFAs are tested in this work, one based on the classical P3HT donor with the acceptor o-IDTBR while the other one is the recently reported highly efficient PM6:Y6 system. Our first attempt to integrate AgNP films as top electrodes for PM6:Y6 solar cells are presented in the supplementary information with the best PCE at 9.4%. On the other hand, printed P3HT: o-IDTBR solar cells are successfully integrated with AgNP top electrodes using various printing techniques. Figure 5 shows the performance characteristics of such devices. The average PCE for fully covered EvapAg reference is 5.9%, which is close to other reported data. Similar to PV2000:PCBM based devices, cells with AgNP electrode have lower Jsc but otherwise perform very similarly to their EvapAg counterparts. The Jsc difference between the two electrode types is about 7.7%, which is slightly larger than in the case of PV2000:PCBM. The spectral responses of both types of PALs are also very similar (Figure S4, Supporting Information), except the gap between both electrode types being smaller.

Besides opaque solar cells, printed semitransparent cells were also fabricated with conventional current collecting grids.
Figure 4. Performance data of 0.1 cm² PV2000:PCBM cells with 200 nm EvapAg and doctor blade coated AgNP top electrodes with different thicknesses that are measured under 1000 W m⁻² and 16 W m⁻² for an AM1.5G spectrum; a) PCE; b) $J_{sc}$; c) FF; d) $V_{oc}$; e) current density @ 1.2 V; f) leakage current density @ −0.5 V. Data which are collected under 16 W m⁻² are separated by a vertical line and are indicated by dashed box plots. Typical current voltage characteristics of cells fabricated with different AgNP film thicknesses for Y-axis up to g) 40 mA cm⁻² and h) 280 mA cm⁻² to show the high injection region in order to compare their series resistances.
combined with highly conductive PEDOT:PSS (FHC Solar). This is done to minimize the difference in reflectance between EvapAg and AgNP electrodes so that the process compatibility of top electrode deposition can be compared. However, the printed AgNP grid turns out to have slightly wider than its evaporated counterpart (~100 nm vs 150 nm), resulting in slightly higher $J_{sc}$ (~0.5 mA cm$^{-2}$). This gain is somewhat counteracted by the slightly higher FF for EvapAg cells, which in turn is due to the lower grid resistance of EvapAg compared with AgNP. This is further illustrated by the difference in injection current density under high forward bias in Figure 5e. Moreover, the difference in $J_{sc}$ between opaque and semitransparent cells is only around 1 mA cm$^{-2}$. This is due to the relatively high absorbance of the PAL, which diminishes the effect of the back reflector.\[45]
Overall, this work shows that this formulation can be inkjet printed and the device with printed grids has very similar performance as evaporated ones as reflectivity is no longer a critical parameter.

2.4. High Efficiency OPV Module with Printed AgNP Electrode

Finally, to test the compatibility of AgNP electrodes with modularization, a series of 4cm² PV2000:PCBM test modules is fabricated. The PV2000:PCBM is chosen for its wide availability and abundance of cross-reference module performance data. The module fabrication follows the standard ultrafast LASER patterning procedure described in detail in previous works.[38,48,49,59-63]

One issue that arises from the excellent conductivity of AgNP films is the relative ease of shorting the cells during top electrode patterning. Whiskers or flakes of the AgNP film that remain after patterning can dip into the P2 groove, forming a bridge between the top and bottom electrode. However, this issue can be circumvented by patterning the top electrode before the sintering step. When individual AgNPs are not yet fused, the film adhesion as well as reflectance are much lower, which facilitates removal by LASER.

The module layout for modules with AgNP electrodes is shown in Figure 5a, Supporting Information. A relatively conservative module layout is designed, which results in a GFF of these test modules at only 89% for 4 cells with each cell having 4.4 mm in width and 20 mm in length. This is done to improve the yield so that module reliability can be compared better. The GFF can be increased by reducing the safety margin between the patterning lines. Similar to the previous sections, modules with EvapAg top electrode are also fabricated as a reference for comparison. The layout for AgNP modules is shown in Figure 5b, Supporting Information. Due to the previously described issues with shorts during patterning, the top electrode is fabricated with evaporation masks instead. This has incurred a significant loss in active area with the GFF at only 80% due to additional mask alignment and process limit of thermal evaporation, which provides AgNP electrodes with an additional advantage in terms of scalable processing over EvapAg. Three devices are fabricated for each condition in this experiment. Their current voltage characteristics and performance data are provided in Table 4.

The maximum PCE for modules with AgNP electrode is 7%, which is the highest reported value in literature for organic solar modules with printed top electrode. Considering the best PCE for modules with EvapAg is 7.29% in this work (highest reported value in literature is 7.56% from[46] by the manufacturer), the difference between the printed and evaporated electrode is only 4%. Similar to results for cells with printed AgNP, the majority of loss originates from reduced $J_{sc}$ while other parameters are almost the same. Furthermore, modules with thicker AgNP films in general (>150 nm) perform almost as good as the 0.1 cm² cells in Figure 4. This proves experimentally that the performance loss in modularization can indeed be minimized by high performance top electrodes and rational module layout design.[35,36]

The OPV modules with thinner AgNP top electrode thicknesses (<150 nm) however reveal a very different result. The PCE, FF and injection current density are significantly lower than the reference module with EvapAg as well as test cells in Figure 4. Furthermore, the FFs of the modules are increasing with AgNP electrode thickness, which is not the case for the test cells. The results in Figure 6a,b are also different from those in Figure 4g,h as the series resistance of the modules with thinner AgNP films are clearly higher than those of cells with the corresponding electrode thickness. Given all the results presented, the additional electrical resistance must come from the additional interconnections between individual cells. To understand why some samples suffer from higher interconnection resistance than the others, dark lock-in thermography (DLIT) is performed on the two modules with the smallest and the largest AgNP top electrode thicknesses, i.e., 100 and 300 nm. The DLIT is a measurement technique to locate localized defects and discrepancies on a relatively large device area. The detailed operation of DLIT can be found in our previous works.[64-67] In summary, DLIT uses a pulsed, amplitude modulated electrical pulse to excite periodic thermal signals in the sample, which is then observed by a locked-in IR camera. In this work, the modules are under high forward bias to investigate their local resistance hkes.[66] The thermal images in Figure 6c,d have indicated a stark contrast between the two modules. While the interconnection line for the module with 300 nm thick AgNP top electrode is mostly uniform and continuous, the 100 nm equivalent is discontinuous and inconsistent. This phenomenon is best illustrated by the schematic in Figure 6e. When the top electrode is too thin, there are insufficient AgNPs to fill the P2 interconnection grove. This causes the AgNP film to “pinch off” in localized areas at the interconnection region, which results in localized higher current density that increases the effective interconnection resistance. The random nature of this issue also explains the seemingly quite varied FF and injection current density for the supposedly identical device, which is gradually diminished as the top electrode thickness increases. Overall, despite the fact that the maximum PCE is achieved with a 210 nm thick electrode, 300 nm appears to be the most reproducible at a slight cost in PCE and $J_{sc}$. This issue is dependent on the overall device stack thickness and will be alleviated as the PAL of newer material systems tend to have lower optimal thicknesses.

3. Conclusion

By meticulous design and optimization in both ink formulation and processing, low temperature sinterable AgNP electrodes deposited by doctor blade coating can achieve very similar optical and electrical performance as those prepared with EvapAg. While the latter are the exclusive type of electrode used for record efficiency lab cells, AgNP electrodes are compatible with low temperature R2R printing processes, which are essential for high throughput manufacturing of OPV. We have confirmed experimentally that AgNP and EvapAg electrodes provide almost identical results for three different material systems, each representative of the broad varieties of PALs developed over the past decade. Moreover, it has also been experimentally proven that cells with AgNP electrode perform even better than those with EvapAg under low light conditions, due to their much lower leakage current.
Figure 6. Current voltage characteristics of best performing module in a batch of 3 samples with the same top electrode. The Y-axis is up to 40 mA cm\(^{-2}\) for a) and up to 280 mA cm\(^{-2}\) for b) to show the high injection region in order to compare their series resistances; DLIT amplitude image of organic solar modules under high forward bias, \(V_{\text{amp}} = 4.8\) V, \(f_{\text{li}} = 1\) Hz, 10 000 periods; c) 100 nm AgNP top electrode; and d) 300 nm AgNP top electrode. The interconnection region is indicated by the white arrows; f) schematic cross section of PV2000:PCBM module with AgNP top electrode. Inset shows the enlarged and exaggerated contact region between the P2 interconnection and the top electrode. While the PEDOT:PSS layer underneath is also somewhat conductive, the added resistance, even in milliohms range will significantly affect the module performance as illustrated by our previous work\(^{[12]}\). No such issue has been observed for devices with EvapAg.
### Table 4. Performance data of the best OPV modules in Figure 6. The average values are given in parentheses.

| Active area $J_{SC}$ [mA cm$^{-2}$] per cell | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] per cell | FF [%] | Active area PCE [%] | Injection @ 4.8 V [mA cm$^{-2}$] |
|------------------------------------------|-----------|-------------------------------|-------|----------------------|---------------------------|
| EvapAg                                   | 14.76(14.50) | 3.01(3.00) | 0.75(0.75) | 0.66(0.65) | 7.29(7.1) | 161.1(166.96) |
| $\approx$100 nm                           | 13.93(13.28) | 2.86(2.81) | 0.72(0.70) | 0.47(0.40) | 4.53(3.58) | 33.1(19.7) |
| $\approx$150 nm                           | 13.27(13.72) | 2.94(2.92) | 0.74(0.73) | 0.56(0.54) | 5.32(5.21) | 57.2(60.22) |
| $\approx$210 nm                           | 14.05(14.04) | 3.07(3.07) | 0.77(0.77) | 0.63(0.62) | 7.00(6.83) | 177.4(132.42) |
| $\approx$300 nm                           | 13.20(13.31) | 3.10(3.09) | 0.78(0.77) | 0.64(0.63) | 6.52(6.48) | 138.6(128.14) |

This work has also demonstrated experimentally that the efficiency loss upon upscaling organic solar cells to modules can be significantly reduced by AgNP grid top electrodes. This makes them the ideal choice for high throughput R2R printing of OPV modules, for which so far only transparent top electrodes have been available, namely screen printed silver grid electrodes and slot die-coated AgNW mesh electrodes. In contrast to screen printed silver grid electrodes, AgNP electrodes are compatible with LASER patterning, which allows high GFF organic solar modules to be fabricated by this type of electrode.

The AgNW meshes show low reflectivity, which cause low $J_{SC}$ and limited conductivity, which compromises FF. These factors severely limit the performance of fully printed OPV modules. The advantages of the AgNP electrodes presented in this work, namely high reflectivity, high conductivity, and good process compatibility with OPV fabrication have resulted in printed organic solar modules that are much better in performance than previously reported. This work has demonstrated a fully printed PV2000:PCBM module with 7% PCE, which is almost 3% more than the analogous module with AgNW electrodes and is only 0.5% different from best performing OPV modules with EvapAg.

This work has provided a promising alternative to the available top electrode selection in organic photovoltaics. As the efficiency of OPV devices, especially their $J_{SC}$ continues to rise, the tradeoff for semitransparency may no longer be acceptable in many applications. By forgoing semitransparency for device performance, full area AgNP electrodes are particularly useful for applications where semitransparency is not an important factor or simply not needed, such as indoor light harvesting or photovoltaics that are directly attached to the load like solar backpacks or facades.

### 4. Experimental Section

**Materials:** Technical grade P3HT, technical grade PCBM, technical grade PV2000, and O-IDTBBr were purchased from BASF SE., Solenne BV, Raynergy Inc. and Nano-C Inc. respectively. The PM6 and Y6 were kindly provided by professor H. L. Yip from SCUT, China. Poly(3,4-ethylenedioxythiophene) poly(styrene sulphonate mixture (PEDOT:PSS), Clevis HTL Solar, FHC Solar, Clevis P VP AI 4083, were purchased from Heraeus Holding GmbH. The ZnO nanoparticles (ZnONP) dispersion (N)–10 was purchased from Avantama. The UV curable epoxy Delo-KatioBond LP655 was purchased from DELO Industrial Adhesives. AgNP paste DF-AT-2011 was supplied by Dowa Electronics Materials co. ltd. The AgNP ink Sicrys 40DM-106 and EMD5800 were purchased from PV Nanocell Ltd. and Sun Chemical Ltd., respectively. All solvents used in this work are above 99% purity and were purchased from Sigma-Aldrich Corporation. All the materials were used as received without further purification. The ITO-coated glass substrates with a sheet resistance of 12 $\Omega \cdot \text{cm}^{-1}$ and transmittance of 81% at 550 nm were purchased from VisionTek Systems Ltd. and LASER patterned in-house.

**Solution Preparation:** The AgNP dispersion ink was prepared by 3 consecutive dilution steps from its paste formulation. In each step, solvent was added then stirred vigorously, followed by centrifugal mixing for 1400 rpm for 20 s. The 3, 16, and 50 wt% of solvent were added in each step of dilution. The ink was then ultrasonicated by an ultrasonic homogener for 1 min followed by filtering with 1um syringe filter with glass fiber membrane. The ink can be stored at 4–6 °C when not in use for up to 1 month. The inks were ultrasonicated in an ultrasonic bath for 5 min before use.

The ZnO nanoparticle dispersions were filtered with 0.45μm PVDF filter before use. The P3HT and O-IDTBBr were dissolved in a mixture of O-xylene (95% vol) and 4-Bromoanisoile (5% vol), each at 10 mg mL$^{-1}$. The PV2000 and PCBM were dissolved in O-xylene at 14 and 21 mg mL$^{-1}$, respectively. The mixture was stirred overnight at 60 °C and cooled down before use. The PM6 and Y6 were dissolved in chloroform at 8.33 and 8.33 mg mL$^{-1}$ respectively and then stirred at room temperature. The PEDOT:PSS printing solution was prepared by dilution of pristine PEDOT:PSS with DI water at 1:1 ratio. 0.1 vol% (0.2 vol% for AI 4083 and 0.5 vol% for FHC solar) of fluorosurfactant Capstone FS-31 and 0.05 vol% of Silane Silquest A-187 were subsequently added and mixed.

**Equipment Used:** The doctor blade (Model ZAA2300) and applicator (Model ZUA 2000) are from Zehntner GmbH. Laser patterning is performed by LS-6K4P520 from LS Laser Systems GmbH equipped with a Spirit 1040-8-SHG from Spectra Physics (Rankweil, Austria) emitting at 520 nm with a pulse duration of 350 fs at repetition rates up to 960 kHz. Thermal evaporation is done in a Oerlikon Leybold UNIVEX 250 system.

Characterization of the solar cells and modules were performed with LS9016 AAA solar simulator from LOT quantum design. The power output was calibrated prior to the measurement using a reference monocrystalline silicon solar cell from the same company. Diode current voltage characteristics were obtained from B2901A sourcemeter from Keysight Technologies Inc. The current from the device was measured when the voltage range swept from $-1$ to 1.5 V using 20 mV steps for cell devices while the voltage range swept from $-2$ to 6 V using the same voltage steps for modules. All device areas were confirmed by confocal microscope jsurfs custom from NanoFocus AG. Transmittance data were acquired with a Lambda 850 UV/VIS Spectrometer from PerkinElmer Inc. Transmission spectra were recorded from 300 and 850 nm with a step size of 1 nm using an integrating sphere.

The SEM images were obtained from JSM-7610F from JEOL, Ltd. Sheet resistance of films were measured by a noncontact sheet resistance meters from Delcom Instruments Inc. Film thicknesses were measured by Alpha-Step D-100 Stylus Profiler by KLA-Tencor Inc. Individual film thicknesses of all cells and modules are checked to ensure they have roughly the same film thicknesses during fabrication. The DLIT is performed using a Taurus Taurus 110 k SM pro IR-camera from IRCAM GmbH controlled by a computer that performed all lock-in calculations. The IR camera is equipped with a cooled indium–antimonite and focal plane array detector (384 × 288 pixels) with a noise equivalent temperature difference of less than 20 mK. The IR detector is highly responsive in the spectral range between 2 and 5 μm and provides a frame rate of 100 Hz. For all
measurements, the lock-in frequency was set to 1 Hz in order to minimize implications due to the heat diffusion length. A power supply is used as a pulse source, which is measured with a standard digital multimeter. The EQE spectrum were recorded with an IPCE Measurement System QE-R from Enli Technology, which was also calibrated with a standard single-crystal silicon solar cell. The spectrum is measured between 300 and 850 nm using a step size of 10 nm.

Device Fabrication: All substrates used in this work were ultrasonicated with isopropanol and toluene consecutively for 5 min. All layers are doctor blade coated unless otherwise stated. The ZnO was coated at 5 mm s^{-1} 30 °C at 400 μm gap to achieve 40 nm film thickness. The film was then annealed again at 200 °C for 5 min. Different PALs were coated at different conditions for different material systems. The PV2000:PCBM was coated at 30 mm s^{-1} 65 °C at 400 μm gap to achieve 250 nm film thickness. The P3HT:o-IDTBR was coated at 33 mm s^{-1} 65 °C at 400 μm gap to achieve 250 nm film thickness. The PM6:Y6 was coated at 20 mm s^{-1} 30 °C at 400 μm gap to achieve roughly 150 nm film thickness. The HEL was coated at 10 mm s^{-1} 65 °C at 400 μm gap to achieve roughly 150 nm film thickness. For grid devices, FHC solar was ink-jet printed at 600 DPI at room temperature and then subsequently dried at 65 °C. Then, the samples were annealed at 120 °C for 5 min inside the glove box. The AgNP electrodes were coated on samples with either doctor blade coating or inkjet printing. Full area electrodes were doctor blade coated at 65 °C at 400 μm gap while inkjet-printed grids were printed on top of HEL at 400 DPI at room temperature and then subsequently dried at 70 °C. The AgNP electrodes were then laser structured the same way as in the P3 step shown below. The samples were then annealed inside the glove box again to form a conductive electrode. Samples with EvapAg were coated in evaporator under pressure < 6 × 10^{-6} bar for 200 nm at a rate < 0.05 nm s^{-1}.

For module fabrication, ZnO layer, PAL and PEDOT:PSS layers were coated at the orthogonal direction to the ITO direction to minimize the impact of film thickness variation with respect to the coating direction. The P2 structuring was performed with femto-second laser at 500 mm s^{-1} at ~1 W after HEL deposition. The P3 structuring was done at 1000 mm s^{-1} at ~1.3 W after AgNP deposition. The samples were then blown clean with compressed air before annealed inside glove box at 140 °C for 5 min. Both cells and modules samples were then encapsulated by adding a barrier glass on top of the device with the UV curable epoxy Delo-Katiobond LP655 for 2 min.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the authors.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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