

Evaporation-Free Organic Solar Cells with High Efficiency Enabled by Dry and Nonimmersive Sintering Strategy

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A solution-processed top electrode is critical to unlock the full potential of all-solution-processed organic solar cells (OSCs) for practical applications. However, the enabled devices suffer from low efficiency (<12%) mainly because of the irreversible damages induced by the top-electrode deposition process. Herein, a strategy of dry and nonimmersive sintering is demonstrated by introducing a hydrogen-intercalated molybdenum oxide layer to sinter isolated Ag nanoparticles into the top electrode (all from solution process) with little influences/issues on underlying device structures. Fundamentally, it is unveiled that the intercalated hydrogen will bond with the amino group of the ligands around Ag nanoparticles, which promotes the exposed nanoparticles to merge along a certain crystal orientation ($\approx 45^\circ$) and form a conductive electrode ($8.6 \Omega \text{ sq}^{-1}$). Importantly, the sintered electrode offers 70% optical reflection in the 700–1050 nm wavelength region, which is essential to enhance the light absorption of high-performance nonfullerene acceptors. Consequently, a record efficiency of 15% is achieved, driving all-solution processed OSCs toward commercial applications.

power conversion efficiency (PCE) of less than 12%, which is far below the devices with evaporated electrodes.^[3–5] Such a low efficiency is ascribed to the fact that, during solution deposition process, the detrimental solvents, high temperature or mechanical force applied will exert on the whole device to cause material dissolution, corrosion, and/or poor inter-layer contact, which finally deteriorate the OSC photovoltaic performances.

The typical solution-processed electrodes mainly involve carbon materials, conductive polymers and metal electrodes. Carbon materials including graphene and carbon nanotubes usually suffer from high resistance because of the low intrinsic carrier concentration or poor inter-tube contact.^[6–8] Conductive polymers such as Poly(2,3-dihydrothieno-1,4-dioxin):poly(styrenesulfonate) (PEDOT:PSS) have shown good flexibility and conductivity.^[9,10] Nev-

1. Introduction

Solution-processed top electrode plays a critical role to eliminate the incompatible evaporation process in achieving high throughput OSCs fabrication via all-solution processed approaches such as roll-to-roll process. The enabled OSCs diversify the low-cost and emerging power applications such as solar windows and wearable electronics.^[1,2] However, the current fully solution-processed OSCs have only achieved a

ertheless, the strong light absorption and terrible wetting issue is of great concern when employed as top electrode in OSCs.^[5]

Metal electrodes such as Ag nanowires (Ag NWs) and silver pastes have exhibited excellent conductivity and ductility. Ge and co-workers reported a Ag NWs film with a low sheet resistance of $13 \Omega \text{ sq}^{-1}$ and good bending properties after removing Poly(vinylpyrrolidone) (PVP) ligand.^[11] To ensure good connection between metal media, a wide variety of post-treatment methods such as thermal annealing^[12,13] and light induced sintering^[14,15] have been adopted to weld Ag NWs and Ag nanoparticles (Ag NPs) after the pre-deposition. However, these harsh/rigorous post-treatments will act on the whole device and potentially degrade the organic active layer. Meanwhile, solution-involved post-treatments such as chemical welding have been used to effectively weld or sinter Ag NWs^[16] and Ag NPs.^[17] Though excellent conductivity can be achieved at room temperature, the metal nanomaterials have to be fully immersed into chemical solution for seconds or even hours^[18] to ensure good chemical reaction, which inevitably causes the dissolution of underlying functional layers and deteriorate the OSC efficiency. For example, in our previous work,^[19] Ag NPs electrodes are required to fully immerse into a chemical solution that contains an oxidizing agent, AgNO_3 , which can easily destroy bottom device even at a low concentration of 0.02 M. The optimized device exhibits lower fill factor (FF) than the evaporated counterpart, suggesting an increased surface

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recombination. Lamination or transformation process have been successfully applied to avoid the post-treatment effect and detrimental solvents in the metal precursor solution.^[20–22] For instance, Yusoff and co-workers laminated their Ag NWs on top of tandem solar cells by applying 1.4×10^4 psi uniaxial pressure and achieved a PCE of 8%.^[22] Nevertheless, such a high mechanical force will exert on the whole device and the electrical contact shall be addressed between the laminated top electrode and the bottom device to ensure good inter-layer carrier transportation.

In addition to the degradation/destruction of OSCs induced by the electrode deposition process, another reason that limits the photovoltaic performance of fully solution-processed OSCs is the insufficient light absorption especially for the overwhelming nonfullerene-based devices. Nonfullerene acceptors have strong absorption in near infrared range, which compensate the donor absorption and contribute to the overall device photocurrent. Unfortunately, compared to evaporated metal electrodes, solution-processed transparent top electrodes including Ag NWs, metal grids, PEDOT:PSS and graphene have typically sacrificed the second light pass due to the low reflection for these electrodes, leading to lower short-circuit current (J_{sc}). For example, Nie et al. reported a fully solution-solution processed OSCs employing a modified PEDOT:PSS as top cathode.^[23] The device delivered a PCE of 11.12% with contrast to 13.42% of its evaporated counterpart. The major difference stems from the J_{sc} (19.55 mA cm^{-2} and 22.66 mA cm^{-2} for solution process and evaporation, respectively). Therefore, a solution-processed top electrode that enables good interfacial contact, negligible influence on other layers and sufficient light absorption is strongly favoured and needed.

In this work, we demonstrated a dry and nonimmersive sintering (NIS) approach to sinter isolated Ag NPs by a hydrogen-intercalated molybdenum oxide (HMO) layer for forming solution-processed top electrode in OSCs. The hydrogen-induced sintering mechanism is newly developed and are systematically studied. As disclosed, the intercalated hydrogen will first bond with the amino group of the ligand around Ag NPs. Subsequently, the coordinate bond between the Ag NPs and ligand will be broken and the exposed Ag NPs will merge to each other at a certain crystal orientation. Because of the intrinsic inter-particle connection, a smooth and compact electrode with low root mean square roughness (R_{RMS}) of 2.313 nm and sheet resistance of $8.6 \Omega \text{ sq}^{-1}$ is achieved. Unlike other solution-processed top electrode, the NIS process avoids immersing the electrode into a solution and circumvents other detrimental post-treatments such as high-temperature annealing, which preserves the photoelectrical properties of the underlying functional layers. Importantly, the sintered continuous Ag film offers 70% light reflection in red to near infrared spectrum (700–1050 nm), which overlaps with the absorption spectrum of many nonfullerene acceptors and ensure sufficient light absorption of the active layer. Benefiting from the excellent electrode film quality together with negligible influence on other layers, the fabricated devices achieve a record average and best PCE of 14.5% and 15.0%, respectively, outperforming other OSCs with a solution-processed top electrode.

2. Results and Discussion

Figures S1 and S2 in the Supporting Information shows the crystal structure and morphologies of the synthesized Ag NPs and HMO, the detailed discussion of the results is provided in the Supporting Information. After thermal reduction of AgNO_3 , oleylamine capped Ag NPs with 6-nm diameter and cubic crystal have been successfully obtained (Figure S1, Supporting Information). The as-synthesized HMO is amorphous with a $\text{Mo}^{5+}/\text{Mo}^{6+}$ ratio of 0.18, indicating a chemical formula of $\text{H}_{0.15}\text{MoO}_3$ according to the electrical neutrality law (detailed description is provided in Figure S2 in the Supporting Information). We then deposit HMO layer (thickness around 12 nm) and Ag NPs layer (thickness around 29 nm) to investigate the NIS process. **Figure 1a** shows the ex situ scanning electron microscopy (SEM) images of Ag NPs electrode after different sintering periods (0–60 min). Initially, the Ag NPs display an isolated morphology. With the proceeding of the sintering, the separated particles start to merge together and the particle size increases gradually. Finally, the connected Ag continents with diameter of $\approx 100 \text{ nm}$ are obtained (Figure 1a–60 min). During the sintering process, the sheet resistance of Ag NPs electrode decreases conspicuously from over 10^6 to $8.6 \Omega \text{ sq}^{-1}$ (Figure 1b). The sheet resistance will further decrease with the increase of sintering temperature and finally reaches asymptotic limit of $2.9 \Omega \text{ sq}^{-1}$ at 180°C (Figure S3, Supporting Information), which is much lower than typical ITO electrode (indium tin oxide, $\approx 15 \Omega \text{ sq}^{-1}$) and many other transparent electrodes. Such low sheet resistance can be attributed to the fine inter-particle crystal lattice matching after sintering. Importantly, without the dry sintering layer, Ag NPs film remains highly resistive until a high temperature is employed ($>220^\circ \text{C}$, $>30 \text{ min}$). In addition, the layer thickness of sintered Ag is not necessary to be 29 nm. For Ag NPs with different thicknesses, the sintering time and interface properties shall be re-adjusted and optimized. Generally, thicker Ag NPs and thinner HMO require longer time to fully sinter the electrode as shown in Figure S4 in the Supporting Information.

Figure 1c discloses the isolated NPs before sintering with a crystal lattice distance of 2.36 Å, which can be ascribed to the (111) plane of cubic silver. After sintering, the Ag NPs are intrinsically merged together with the white dashed line marking the interface as shown in Figure 1d, which is completely different from the reported Ag NWs electrode that requires extra chemical solders to ensure wire connection. More importantly, these Ag NPs are sintered through a certain crystal orientation (45°) rather than chaotically stacked together. The better merging between adjacent NPs with certain orientation should contribute to the impressively low sheet resistance of the electrode. Atomic force microscopy (AFM) is used to characterize the film roughness (Figure 1e; Figure S5, Supporting Information). The sintered film presents a low RMS roughness of 2.313 nm, which is even lower than 2.767 nm of evaporated Ag electrode. To further demonstrate the uniformity and scalability of the NIS electrode, we have deposited the NIS-based electrode on substrate with a big area of $5 \text{ cm} \times 5 \text{ cm}$. In different sampling spots (Figure S6, Supporting Information), the electrode presents similar resistance ($\approx 8.7 \Omega$), morphology and RMS roughness ($\approx 2.2 \text{ nm}$), suggesting the solution-processed

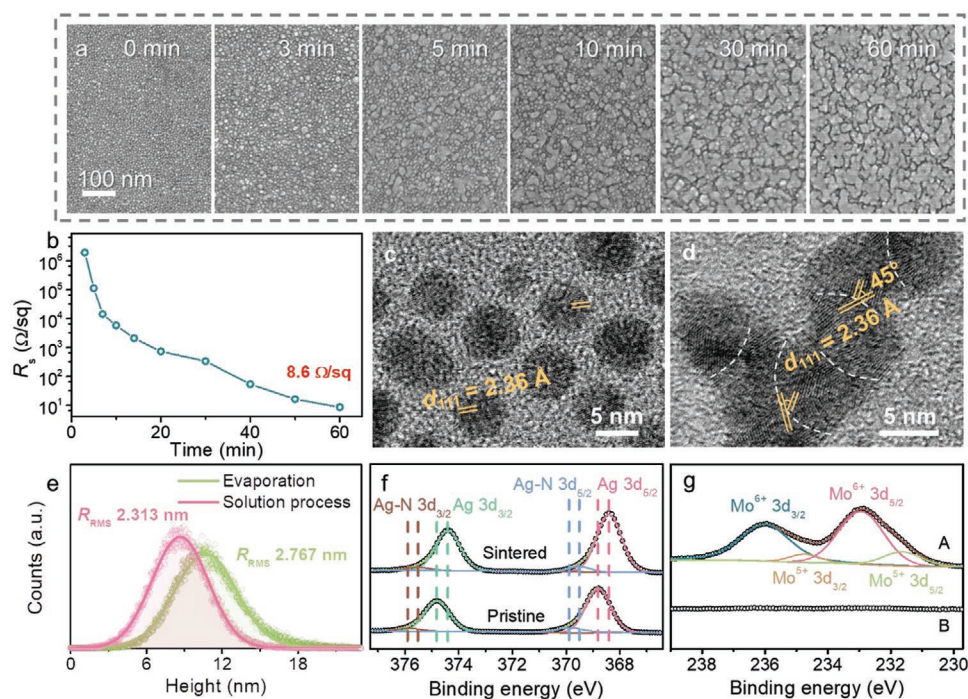


Figure 1. a) Ex situ SEM images of Ag NPs film after different sintering times (0–60 min). b) Sheet resistance of the electrode after different sintering times. Transmission electron microscopy (TEM) images of Ag NPs c) before and d) after sintering. e) The extracted electrodes surface height histogram figure from AFM images. f) Core-level Ag 3d XPS spectra of the electrode in pristine and sintered states. g) Core-level Mo 3d XPS spectra derived from different surfaces (A for HMO surface, B for sintered Ag NPs surface).

electrode is highly uniform in large area. Additionally, this NIS electrode shows excellent adhesion strength. As shown in Figure S7 in the Supporting Information, a tape was stuck on top of the electrode deposited on glass substrate. We can uplift the electrode together with the glass substrate through the tape, suggesting that the tape is firmly stuck on the electrode surface. After removing the tape, the solution-processed electrode remains on the substrate, which confirms the strong adhesion of the electrode to smooth surface to provide efficient charge transportation property.

Figure 1f displays the core-level Ag 3d X-ray photoelectron spectroscopy (XPS) spectra of the electrode in pristine and sintered state. The complete survey spectra are provided in Figure S8 in the Supporting Information. In sintered state, two major peaks sited at 374.4 and 368.4 eV 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 peaks at 375.5 and 369.5 eV can be assigned to nitrogen coordinated silver ($\text{Ag-N } 3d_{3/2}$ and $\text{Ag-N } 3d_{5/2}$).^[27] The corresponding peaks in pristine electrode shift to higher binding energy (0.4 eV) because of the depletion of electrons in valence band with the decreasing particle size.^[25,28] These results further confirm the Ag NPs are well sintered into connected bulk silver. Simultaneously, the Ag–N/Ag ratio significantly decreases from 10.83% to 6.97% after sintering, suggesting a breakage of the Ag–N coordinate bond in the sintering process (Figure S9, Supporting Information).

Figure 1g exhibits the core-level Mo 3d spectra derived from HMO surface (A) and sintered Ag NPs surface (B). There is no obvious Mo signal detected on the sintered Ag NPs surface, indicating that Mo has not permeated through Ag NPs film and

Mo has not participated in the sintering. On the other hand, the peaks refer to Mo^{5+} (234.7 and 231.6 eV) have vanished after annealing at 65 °C for 10 min, implying that HMO ($\text{H}_{0.15}\text{MoO}_3$) have been fully oxidized to MoO_3 (Figure S10, Supporting Information). It is confirmed that the annealed HMO film cannot sinter Ag NPs and the Ag NPs film remains insulated. Therefore, the intercalated hydrogen in the as-synthesized HMO plays a critical role in the sintering process. We have further added 0.12 mol L^{−1} CH_3COOH and 0.12 mol L^{−1} CH_3COOK into the Ag NPs solution to monitor the interaction between H^+ and Ag NPs (Figure S11, Supporting Information). As expected, Ag NPs aggregates and precipitates to the bottom after adding CH_3COOH , while the addition of CH_3COOK has not affected the Ag NPs dispersion. Based on that, we can confirm that H^+ can effectively break the Ag–N coordinate bond and lead to the precipitation of Ag NPs. Moreover, we have also deposited Ag NPs on PEDOT:PSS and phosphomolybdic acid (PMA) dry films that can provide hydrogen ion. As shown in Figure S12a in the Supporting Information, the sheet resistance of both films show drastic decrease from insulation to 8.16 and 33.68 $\Omega \text{ sq}^{-1}$ for PEDOT:PSS and PMA, respectively. A 55-nm thick PEDOT:PSS can effectively sinter 40-nm thick Ag NPs (Figure S12b,c, Supporting Information) and results in a smooth film ($R_{\text{RMS}} = 2.685 \text{ nm}$, Figure S12d, Supporting Information).

According to aforementioned results, we propose the non-immersive sintering mechanism as following (Figure 2). After spin-coating Ag NPs layer and HMO sintering layer, the small amount of intercalated hydrogen from HMO tend to bond with the amino end group of oleylamine, leading to

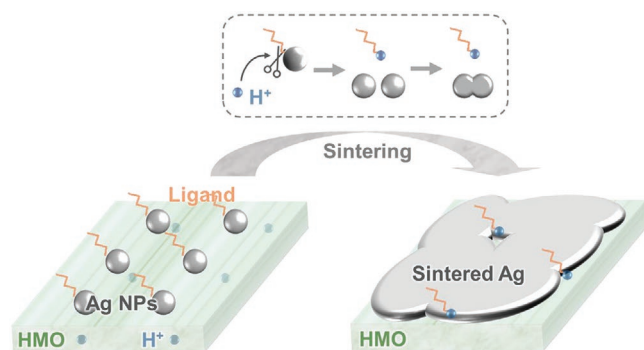


Figure 2. The illustration of the NIS process.

the breakage of the Ag–N coordinate bond and the decrease of Ag–N ratio. After the breakage of the coordinate bond, the Ag NPs are exposed without any organic coating. The adjacent nanoparticles are in direct contact. Despite the weak external force exerted on the nanoparticles (room temperature and dry process), the stress/pressure is very high at the contact area between two nanosized materials with a small contact area, which promotes surface atom diffusion.^[29] During the diffusion process, the adjacent particles that are connected with the same or different crystal planes tend to match well with each other or compensate for different lattice spacing, leading to small mis-orientation between two nanoparticles.^[30] In this work, the sintering proceeds at room temperature and dry condition, the external force is weak, leading to a small mis-orientation of 45° between (111) planes. Such intrinsic inter-particle connection ensures low sheet resistance and thus provide excellent charge transportation efficiency.

We employ the as-achieved electrode to fabricate the OSCs with a conventional device configuration of ITO/PEDOT:PSS/PM6:Y6 (Figure S13, Supporting Information)/ZnO/Ag NPs/HMO. It shall be noted that we adopt the configuration of HMO/Ag NPs in the electrode formation part to directly characterize the morphological evolution of the Ag NPs while it is Ag NPs/HMO in the device fabrication part to ensure that the HMO will not penetrate to bottom layers. As shown in the cross-sectional SEM image (Figure 3a), the Ag NPs are well sintered into a connected and compact film with the HMO decently stacked atop. Importantly, the device preserved its clear and hierarchical structure after top electrode formation. The inset picture of Figure 3a showing the photograph of the fabricated fully solution-processed device. It is worth noting that the sintered Ag NPs electrode offers 70% light reflection in the red to near infrared region (700–1050 nm), which is highly overlapped with the absorption range of the nonfullerene acceptor Y6 as shown in Figure 3b.

To explain the high reflection of the sintered Ag film, we have evaporated Ag electrode with different thicknesses to investigate the relationship between light reflection and layer thickness of continuous Ag film. As shown in Figure S14a in the Supporting Information, when the thickness of the evaporated Ag films increases from 20 to 30 nm, the reflection shows an increasing trend in the visible and infrared region with a high reflection of 68.7% and 78.8% in 700–1050 nm, respectively. Up to the thickness of 100 nm, the reflection is close to 100% in full spectra. The declining reflection trend around 380 nm is ascribed to the absorption of nanosized Ag^[31] (Figure S14b, Supporting Information) and the higher light transmission in this spectrum region. Considering the solution-processed continuous Ag NPs electrode has a thickness of around 29 nm

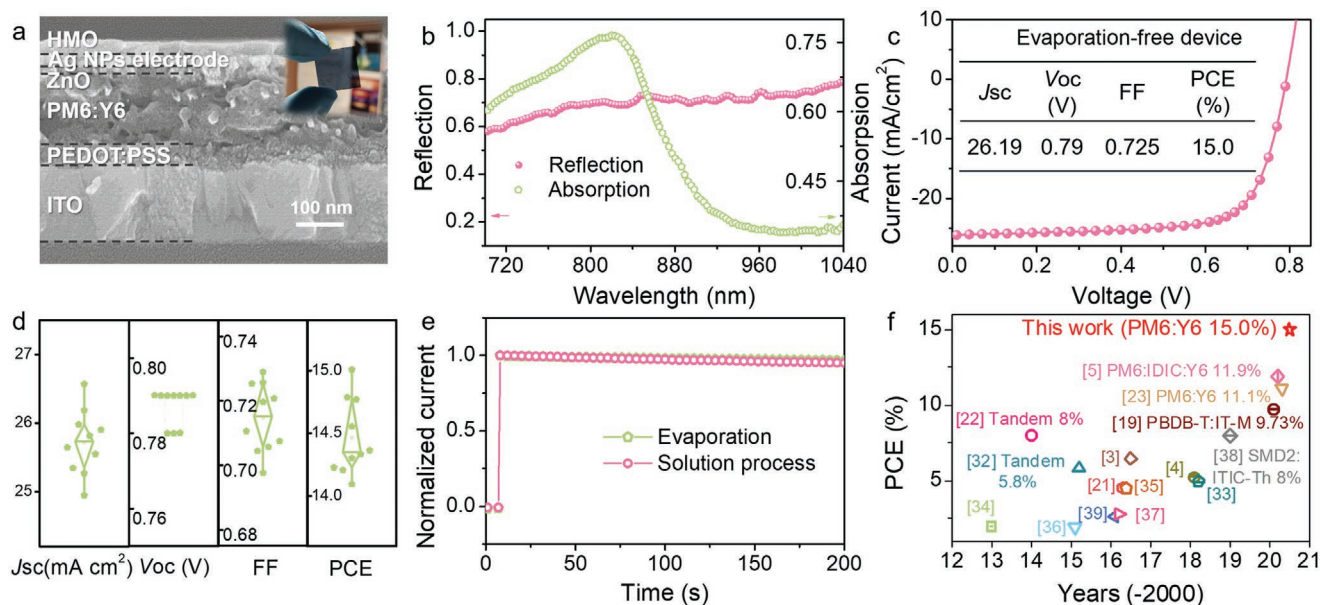


Figure 3. a) SEM image of the evaporation-free device based on the NIS strategy, the inset image shows the device picture. b) The reflection spectrum of the sintered Ag NPs electrode and the absorption spectrum of the active layer in the red to infrared range (700–1050 nm). c) J – V curve of the champion evaporation-free device. d) Photovoltaic parameter statistics of the evaporation-free OSCs. e) Stabilized photocurrent of the evaporation-based and evaporation-free devices at maximum power point. f) The PCE comparison of OSCs between this work and other works with a solution processed top electrode (The active layer materials information of some high performance OSCs are provided).^[3–5,19,21–23,32–39]

(Figure S4a, Supporting Information) and there are narrow gullies in the sintered electrode compared to evaporated electrode (Figure S14cd, Supporting Information), the sintered Ag NPs electrode exhibits a reasonable and high reflection of 70% in 700–1050 nm range. The shallow trough in 450–750 nm is ascribed to the red-shifted absorption of sintered Ag NPs due to size effect. Additionally, the NIS electrode also shows light reflection in visible region (45%), which is beneficial to the absorption of the organic active layer. Figure S15 and Table S3 in the Supporting Information show the J – V performance of the devices with evaporated 20, 30, and 100 nm Ag top electrode, denoted as A20, A30 and A100, respectively. While A20 shows slightly lower average J_{sc} of 23.60 mA cm^{−2}, A30 and A100 present similar J_{sc} of 25.13 and 25.65 mA cm^{−2}, respectively. Those facts sufficiently support that a ≈30 nm continuous Ag film can provide enough light reflection to achieve a comparable J_{sc} to the conventional opaque (100 nm Ag) device in PM6:Y6 based devices.

Since the devices with transparent top electrodes including graphene, PEDOT:PSS and Ag NWs have sacrificed the second light pass, a lower J_{sc} was presented for high-efficiency non-fullerene OSCs fabricated with those electrodes. In contrast, the high reflection of this sintered Ag NPs electrode in the infrared range successfully overcomes this obstacle and enables sufficient light absorption of the active layer. As a result, the fully solution-processed OSCs delivers a PCE of 15.0% with a J_{sc} of 26.19 mA cm^{−2}, open circuit voltage (V_{oc}) of 0.79 V and fill factor (FF) of 0.725, which is comparable to devices with an evaporated Ag electrode (Figure 3c; Figure S16, Supporting Information). The comparable J_{sc} of the device with sintered Ag NPs electrode is ascribed to the high reflection in the infrared range and efficient charge extraction and collection. The slightly lower V_{oc} compared to the reference device originates from the work function change of top electron transport layer (ZnO), which will be discussed later. Additionally, the device performance is highly reproducible with an average J_{sc} of 25.72 mA cm^{−2}, V_{oc} of 0.787 V, FF of 0.715 and PCE of 14.5% for ten individual OSCs. The measurement details of the NIS-based device are provided in Figure S17 in the Supporting Information. As a comparison, the solution-processed devices without HMO dry sintering layer (only Ag NPs layer) exhibit almost no photovoltaic effect with J_{sc} and PCE close to 0 (Figure S18, Supporting Information). Moreover, the stabilized photocurrent of the NIS based OSCs remains 95% of its original value after continuous working at the maximum power point for 200 s, which is almost identical with its evaporated counterpart (Figure 3e). Figure S19a in the Supporting Information presents the stability test of the NIS-based device that stored at glovebox. It exhibits good stability with less than 4% decay of original efficiency after storing for 96 hours in glove box. The corresponding light soaking test is displayed in Figure S19b in the Supporting Information, the device efficiency increases at first 10 min and decreases with further light illumination. It remains 98.7% of its original efficiency after light soaking for ≈40 min.

To prove the achieved results are reliable, we have fabricated the evaporation-free devices in another institute as described in supporting information. The NIS-based device exhibits a PCE of 14.55%, showing the good reproducibility of the NIS strategy

(Figure S20, Supporting Information). The EQE spectrum of the evaporation-free device fabricated in another institute is shown in Figure S21 in the Supporting Information. The integrated J_{sc} with AM1.5 G reference spectrum is 24.1 mA cm^{−2}, comparable to the J_{sc} extracted from J – V curve with little mismatch (24.1 mA cm^{−2}, Figure S20, Supporting Information). The J_{sc} and V_{oc} discrepancy of the evaporation-free devices fabricated in different institutes originates from the raw material (active layer) difference since their evaporated counterparts show identical trend (Figure S16 and Table S3, Supporting Information). To the best of our knowledge, the PCE of our evaporation-free devices outperforms all of the reported devices with a solution-processed top electrode including PEDOT:PSS,^[5,23] Ag NWs,^[3,4,22,32,33] Ag NPs/inks,^[19,34–37] Ag pastes,^[38,39] and graphene^[21] (Figure 3f).

Overall, the NIS process has negligible effect on the underlying functional layers, which is distinct from other solution-processed top electrodes with the same deposition method including commercial Ag pastes, graphite colloidal and welded Ag NWs that will easily dissolve or penetrate the bottom device in the whole device area (Figures S22 and S23, Supporting Information). We have further implemented time-of-flight secondary ion mass spectrometry (ToF-SIMS) on the NIS-based device to investigate the vertical element distribution of various layers. As shown in Figure 4a, the elements from different layers exhibit a decent hierarchical distribution that can be well indexed to the device configuration. Mo element only presents at the top layer in a wide area (150 μm × 150 μm), which is in consistent with Figure 1g that the main framework of HMO (MoO₃) has not diffused to the underlying layers. While MoO₃ has not diffused to the bottom layers, it is critical to unveil the effect brought by the small amount of H⁺ as it promotes the sintering. First, we directly treated the top ZnO layer with CH₃COOH at concentrations varies from 10⁰ to 10³ μmol L^{−1} to uncover the work function (WF) change induced by H⁺ (Figure S24, Supporting Information). The work functions upshift around 0.01 eV after treatment, suggesting its very limited influence on the electron extraction and transportation of the ETL. This work function change also explains the slightly lower V_{oc} of the NIS-based device compared to its evaporated counterpart because H⁺ provided by HMO will affect the work function of ZnO. Such work function change will lead to V_{oc} deviation, which can be found in other reports.^[40,41] Second, it is worth to note that despite the H⁺ has slight effect on device performance, it is controllable during device fabrication. HMO will easily turn into MoO₃ after annealing at a mild temperature (65 °C), indicating the influence from H⁺ is controllable (Figure 1g; Figure S8, Supporting Information).

Furthermore, we have conducted electrochemical impedance spectroscopy (EIS), transient photocurrent (TPC) and transient photovoltage (TPV) measurements on devices with solution-processed and evaporated top electrode to visualize the influence from NIS process on charge extraction and surface recombination. As shown in Figure 4b, the EIS spectra present two arcs in high frequency and low frequency region that corresponds to charge transfer (R_{tran}) and charge recombination (R_{rec}) resistances, respectively. Both spectra can be well fitted with the same equivalent circuit model in the inset of Figure 4b and the fitted result is provided in Table S1 in the Supporting

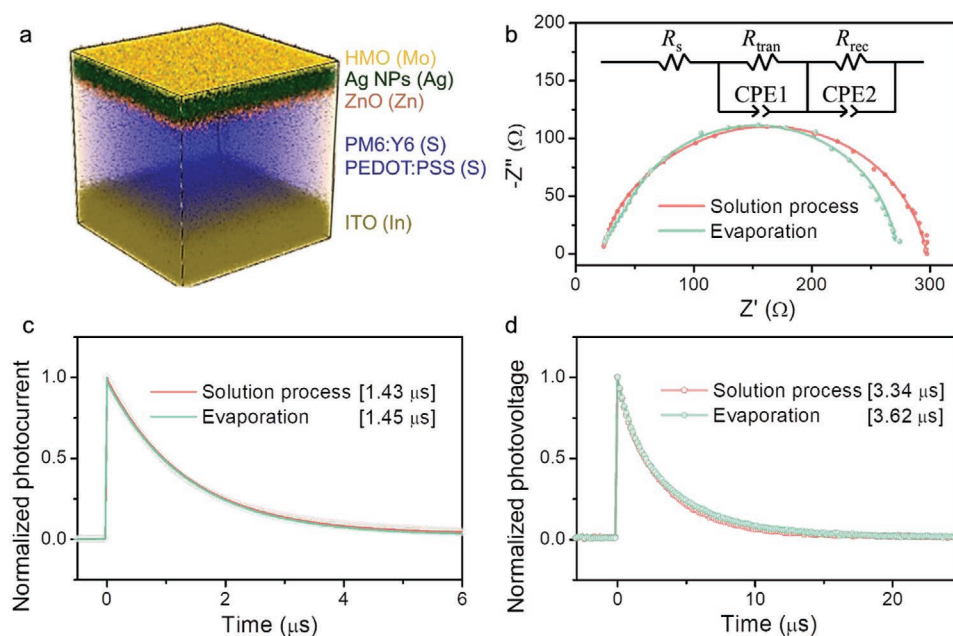


Figure 4. a) ToF-SIMS of the fully solution-processed OSC (the brackets showing the detected elements, measurement area $150\ \mu\text{m} \times 150\ \mu\text{m}$). b) EIS, the inset showing the equivalent circuit model, c) TPC, and d) TPV measurements.

Information.^[42] The evaporation-free device exhibits a low R_{tran} of $13.7\ \Omega$ and high R_{rec} of $260.4\ \Omega$, which is similar to R_{tran} of $9.7\ \Omega$ and R_{rec} $236.8\ \Omega$ for the evaporation-based device. In addition, the evaporation-free device shows a charge extraction time of $1.43\ \mu\text{s}$ (Figure 4c) and carrier lifetime of $3.34\ \mu\text{s}$ (Figure 4d), comparable to the evaporated counterpart (1.45 and $3.62\ \mu\text{s}$, respectively), indicating an efficient charge extraction and suppressed surface recombination of the solution-processed OSCs. All these results suggest that the solution deposition process has imperceptible adverse impact on the OSCs performance.

To prove its wide adaptability, we have applied the NIS approach in other OSC systems with different device configurations. First, we have replaced the PM6:Y6 active layer with another well-recognized nonfullerene based active layer PBDB-T:IT-M (Figure S13, Supporting Information). As given in Figure 5a, the Ag NPs are well sintered into connected electrode and compactly laying on top of the ZnO layer. The champion device yields a PCE of 10.49% with an average PCE of 10% for 8 individual devices (Figure S25a,b and Table S2, Supporting

Information), showing its excellent charge collection properties and reproducibility. Moreover, we have employed this strategy in the fabrication of a fullerene-based benchmark OSC with an inverted configuration of ITO/ZnO/Poly(3-hexylthiophene-2,5-diyl) (P3HT):[6,6]-Phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM)/PEDOT:PSS/Ag. The PEDOT:PSS here functions as hole transport layer and dry sintering layer since PSS can provide small amount of H⁺. A finely stratified structure is captured in Figure 5b. A PCE of 3.7% of the best evaporation-free device is achieved, which is higher than the evaporated counterpart (3.3%, Figure S26a and Table S2, Supporting Information). The better performance originates from the slight WF downshift of PEDOT:PSS after binding with the ligands, which enhance its hole extraction properties (Figure S26b,c, Supporting Information). It is worth to note that the device structure is not immutable, it is also feasible to fabricate fullerene-based device with a conventional structure after proper optimization. The large-area devices ($1\ \text{cm}^2$) are also fabricated with P3HT:PCBM as active layer. It can be seen

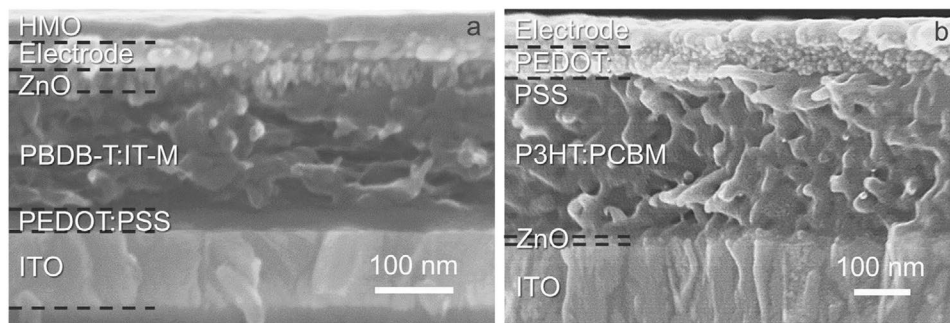


Figure 5. OSCs with the NIS-based Ag NPs electrode. a) Nonfullerene based conventional structure OSC: ITO/PEDOT:PSS/PBDB-T:IT-M/ZnO/Ag NPs/HMO. b) Fullerene based inverted structure OSC: ITO/ZnO/P3HT:PC₆₁BM/PEDOT:PSS/Ag NPs.

from the inset device picture of Figure S28 in the Supporting Information that the NIS electrode is uniformly covered in the whole area. The device exhibits a PCE of 3.12% with a J_{sc} of 9.37 mA cm^{-2} , Voc of 0.60 V and FF of 0.55, which is comparable to its small-area counterpart with a slightly lower FF. The results agree well with Figure S6 in the Supporting Information and shows the scalability and high practical value of the NIS-based electrode.

3. Conclusions

In conclusion, we proposed a new and conceptual nonimmersive sintering strategy that employs a dry film to sinter isolated Ag NPs into well-connected, smooth and conductive electrode. The small amount of H^+ provided by the sintering layer will bond with amino group of the oleylamine ligand and induce the breakage of the coordinate bond between Ag NPs and ligands. The exposed Ag NPs will merge to each other in a certain crystal orientation to form conductive electrode. With such an intrinsic inter-particle connection, a low sheet resistance of $8.6 \Omega \text{ sq}^{-1}$ is achieved. We then adopt this strategy to fabricate fully solution-processed high-performance OSCs. Benefitting from the dry sintering nature, we successfully eliminate the detrimental solvents and post-treatments introduced by other solution-processed top electrodes. Significantly, the employed sintering material (MoO_3) is restricted at the top layer without penetrating to other layers, which in a large extent preserves the underlying functional layers. As characterized, the device presents a charge extraction time of $1.43 \mu\text{s}$ and carrier lifetime of $3.14 \mu\text{s}$, suggesting a suppressed surface recombination as well as efficient charge extraction and transportation. Additionally, the sintered Ag NPs electrode offers a high reflection in near infrared region ($>70\%$), which is different from other transparent top electrodes such as Ag NWs and it satisfies the high absorption requirements of the popular nonfullerene based OSCs. Consequently, the OSCs based on the NIS strategy exhibit a high efficiency of 14.5% (average) and 15% (best), surpassing other reported OSCs with a solution-processed top electrode. This conceptual and simple strategy lifts the performance of evaporation-free OSCs to a new stage toward their commercialization.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

nonimmersive sintering, organic solar cells, silver nanoparticles, solution process, top electrode

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