

Guided-Growth Ultrathin Metal Film Enabled Efficient Semi-Transparent Organic Solar Cells

Yuniu Zhang, Jiawei Zheng, Zhengyan Jiang, Xinjun He, Jinwook Kim, Luhang Xu, Minchao Qin, Xinhui Lu, Aung Ko Ko Kyaw,* and Wallace C. H. Choy*

Semi-transparent organic solar cells (STOSCs) have great potential in power-generating windows for building facades and automobiles. At present, the evaporated metal thin film is widely used as the transparent top electrode in STOSCs owing to its relatively high conductivity. However, its transmittance in the visible range is sacrificed for fulfilling the thickness requirement of the electrical percolation threshold. Herein, a facile approach of introducing pre-located Ag nanoparticles (NPs) with an optimized amount of ligands is demonstrated to promote the high-quality and ultrathin evaporated Ag film formation for high-performance transparent electrodes beyond that of merely evaporated electrodes. With the pre-located and ligand-optimized Ag NPs, the growth of evaporated Ag clusters can be guided to form high-quality transparent electrode. Equally important, the approach also reduces the mis-stacking defects of the electron transport layer and thus favors the carrier transportation/extraction to the electrode. By using these Ag NPs/7 nm Ag with a sheet resistance less than $15 \Omega \text{ sq}^{-1}$ and average transmittance of 59.30% in the visible region as the main structure in the top electrode, a PM6:L8-BO based STOSC achieves light utilization efficiency of 4.422% with a remarkable power conversion efficiency of 12.80%. This work provides a facile strategy to not only realize high-quality and transparent ultrathin electrode with detailed understanding, but also to promote the practical applications of semi-transparent photonic devices.

1. Introduction

Organic solar cells (OSCs) have received tremendous attention from the research community and industry owing to the tunable optoelectronic properties and solution processability of organic semiconductors, lightweight, mechanical flexibility, and semi-transparent nature.^[1,2] Recent breakthroughs in designing conjugated polymer donors and non-fullerene acceptors (NFAs) started a new era of organic photovoltaics, achieving power conversion efficiency (PCE) $\approx 19\%$.^[3,4] With the rapid development of OSCs, semi-transparent organic solar cells (STOSCs) have become a potential candidate for power-generating windows applied in building-integrated photovoltaics (BIPV) and automobiles, by replacing top opaque electrode with transparent electrode. The overall performance of STOSCs should be considered in both optical and electrical assessments. Recent reports on STOSCs applied light utilization efficiency (LUE, determined as $\text{PCE} \times \text{AVT}$) to reflect the trade-off between average visible transmittance (AVT) and PCE, and to make a fair comparison of overall system efficiency. There are different advances in active materials

to improve the performances of STOSCs including applying multicomponent active layer,^[5–7] adjusting donor/acceptor ratio and structure of active layer,^[8–12] and designing near infrared (NIR) absorption active materials.^[13–16] These strategies assist STOSCs to achieve remarkable NIR photon utilization efficiency and high transparency in the visible range.

In addition to the active layer, the transparent top electrode with high conductivity, low absorption, and low reflection in the visible range is a critical component for high-performance STOSCs. Meanwhile, the realization of a simple fabrication process without degrading the underneath structure and a plain structure are highly desirable for promoting facile, low-cost, and practical applications of top electrodes and thus STOSCs. In the past decade, several materials have been developed to replace evaporated metal and applied as electrodes in OSCs, such as conducting polymers,^[17–19] metal nanowires/nanoparticles (NWs/NPs),^[20–25] graphene^[26–29] and carbon nanotubes (CNTs).^[30–33] Among different transparent

Y. Zhang, J. Zheng, Z. Jiang, X. He, J. Kim, W. C. H. Choy
Department of Electrical & Electronic Engineering
The University of Hong Kong
Pokfulam Road, Hong Kong, Hong Kong SAR 852, P. R. China
E-mail: chchoy@eee.hku.hk

Y. Zhang, A. K. K. Kyaw
Guangdong University Key Laboratory for Advanced Quantum
Dot Displays and Lighting
Department of Electrical & Electronic Engineering
Southern University of Science and Technology
Shenzhen 518055, P. R. China
E-mail: aung@sustech.edu.cn

L. Xu, M. Qin, X. Lu
Department of Physics
The Chinese University of Hong Kong
Shatin, Hong Kong SAR 852, P. R. China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aenm.202203266>.

DOI: 10.1002/aenm.202203266

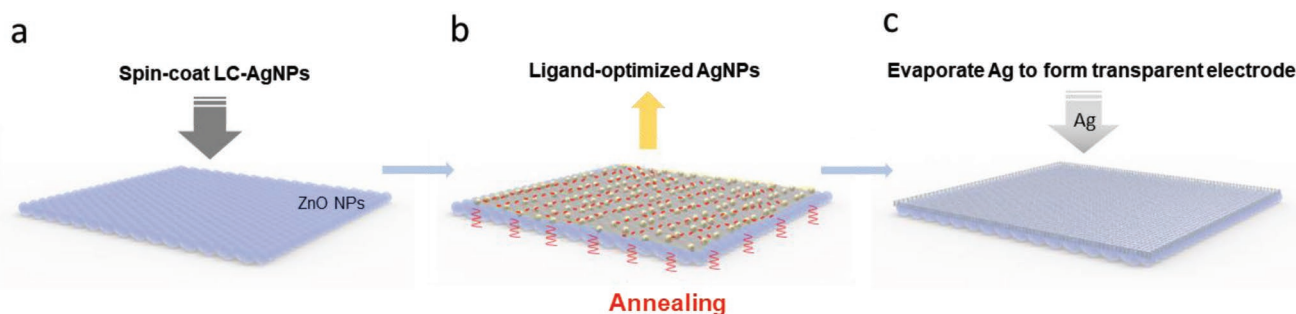


Figure 1. a–c) Scheme illustration of preparing guided-growth ultrathin Ag on ZnO NPs film.

electrodes, evaporated thin Ag film is still frequently used in STOSCs owing to the low electrical resistivity and optical loss in the visible range.^[34] The formation of evaporated thin Ag film usually goes through three steps^[35]: 1) the nucleation and growth of dispersed nanoscopic clusters, 2) coalescence between clusters and formation of nanonetwork at the percolation threshold, 3) increasing metal thickness and the formation of the continuous metal film. Normally, there are migration and liquid-like coalescence of clusters in step 2 due to the weaker adhesion between the metal and carrier transporting layer of OSCs compared to the strong metal-metal cohesion. Therefore, the threshold thickness of Ag is supposed to exceed 15 nm to ensure high conductivity and enough interfacial contact area underneath the functional layer of STOSCs,^[34–36] which unavoidably limits the AVT of devices. To achieve thin Ag electrode with both good conductivity and high transmittance, strategies such as applying seed layer with other materials,^[37] designing optical structures of dielectric/metal/dielectric (DMD) and other multilayer structures,^[21,38–40] as well as using functional surfactants as a wetting or seeding inducer for improving metal growth^[41–43] have been widely studied. These methods suppress the occurrence or effect of cluster migration and enhance wettability to assist solid-like coalescence of Ag clusters during Ag growth, rendering a conductive and compactable film with a thickness of ≈ 10 nm as the top transparent electrode on OSCs. However, tedious deposition engineering, designated materials and structures in these strategies will degrade the charge transport capability of recently reported efficient NFA-based STOSCs. Therefore, the development of affable ultrathin metal electrode with high transmittance in visible range and facile process without degrading the electrical performance of devices is highly desirable.

Here, we propose a unique strategy to reveal conductive and transparent ultrathin Ag network by introducing pre-located Ag NPs to form high-quality evaporated Ag film. The cluster growth of evaporated thin Ag is guided by pre-locating the appropriate quantity of Ag NPs on the substrate and controlling the amount of capping ligands on Ag NPs. Interestingly, the strategy also reduces the mis-stacking defects of the electron transport layer (ETL) favoring efficient carrier transportation between the active layer and electrode. By using the optimized ultrathin Ag composite electrodes with sheet resistance $< 15 \Omega \text{ sq}^{-1}$ and average transmittance of 59.30%, corresponding STOSCs show comparable fill factor (FF) and open-circuit voltage (V_{oc}) with opaque devices, and higher AVT than STOSCs with directly evaporated thin Ag. With further enhancing the

optical features by depositing a dielectric layer on AgNPs/Ag electrode, the as prepared PM6:L8-BO based STOSCs achieves LUE of 4.422% and remarkable PCE of 12.80%, which is the highest efficiency in the reported STOSCs with LUE over 4%. This work provides a unique and facile strategy to achieve high-quality transparent electrode with a comprehensive understanding and offers the applications of emerging semi-transparent optoelectronic technologies.

2. Results and Discussion

2.1. Ligand-Optimized and Pre-located Ag NPs Promoted High Quality Ag Top Electrodes

Figure 1a–c illustrates the deposition process of guided-growth ultrathin Ag electrode on the film of ZnO NPs, which will serve as ETL in STOSCs described in the next section. The used Ag NPs are synthesized by following our previous work.^[25,44] Different from conventional top transparent electrodes formed by Ag evaporation, we pre-locate the Ag NPs on the ETL film by dynamical spin coating and controlling the amount of ligand (Figure 1b). The pre-locating process and control of ligand amount are particularly important to guide the high-quality film formation of the evaporated Ag (Figure 1c). To our surprise, the new approach of Ag film formation also benefits diminishing the defects of ETL film (as discussed later).

The growth mechanism of ultrathin conductive film is illustrated in **Figure 2a**. Oleylamine acts not only as ligand in the synthesis of Ag NPs, but also as the source of amine functional group to assist the formation of ultrathin Ag film. At the beginning of the deposition process, the amine functional groups on oleylamine (originally capped on Ag NPs and released during the annealing process) donate a lone pair of electrons to the evaporated Ag atoms to create strong coordinate covalent bonds.^[45,46] Therefore, Ag NPs-oleylamine groups exhibit strong adsorption to Ag atoms (from evaporation) to reduce their surface free energy,^[34,47] which is favorable in immobilizing the metal that grows on the ETL film during the nucleation and clustering stages. However, our results find that excess oleylamine occupies the space between Ag NPs which hinders the connection between Ag NPs and evaporated Ag, and causes the formation of Ag clusters at the upper plane than Ag NPs, leading to poor conductivity of the film. As shown in Figure S1a,b, and S1d,e (Supporting Information), films with evaporated ultrathin Ag on unannealed Ag NPs show

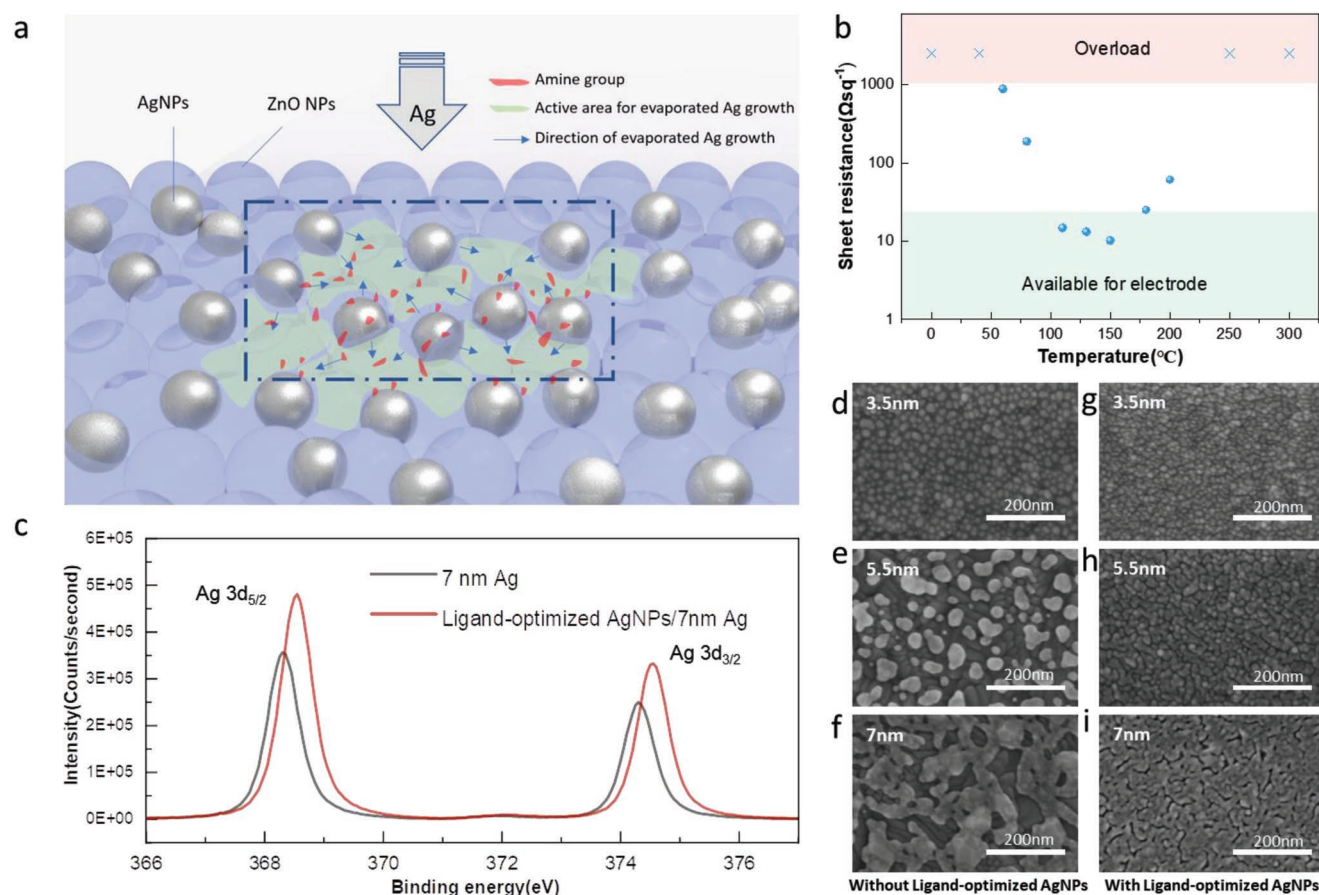


Figure 2. a) Mechanism of guided-growth ultrathin Ag on devices. b) Sheet resistance of films (Concentration of AgNPs: 4 mg mL⁻¹, thickness of Ag: 7 nm) with different annealing temperatures of AgNPs. c) Core-level Ag 3d XPS spectra of ZnO NP film/evaporated 7 nm Ag, and ZnO NP film/ligand-optimized AgNPs/7 nm Ag. SEM images of evaporated 3.5, 5.5, and 7 nm Ag d–f) without and g–i) with the ligand-optimized AgNPs.

non-uniform morphology, and the sheet resistance is too high to be detected (Figure 2b). To address the issue, we introduce a post-annealing process by setting the annealing temperature from 0 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ (0 $^{\circ}\text{C}$ represents an unannealed sample in room temperature) for 10 min on the pre-located Ag NPs followed by Ag evaporation to form Ag NPs/Ag(evaporated) films. The film exhibits sheet resistance higher than 1 M Ωsq^{-1} or even out of detection range when the annealing temperature is lower than 50 $^{\circ}\text{C}$. Interestingly, the sheet resistance remarkably decreases by at least two order magnitudes and reaches lower than 15 Ωsq^{-1} with increasing annealing temperature to 100–150 $^{\circ}\text{C}$, implying that good Ag films are formed at this range of annealing conditions (more evidences will be discussed later). When the temperature increases to over 200 $^{\circ}\text{C}$, the sheet resistance of the film increases to out of detection range again which ascribes to the melt and migration of some Ag NPs into large particles^[48] (Figure S1c, Supporting Information). To verify the change of ligands, we study the atomic percentage of C and N by X-Ray spectrometer (XPS) (Figure S2a,b, Supporting Information). We find that C and N signals significantly reduce after annealing at 100–200 $^{\circ}\text{C}$, implying that 53.5–57.9% oleylamine is removed upon annealing by considering that the ligand is totally removed at the decomposition temperature of oleylamine of 350 $^{\circ}\text{C}$.^[49] XPS spectra of core level Ag 3d are

shown in Figure 2c, the peaks at 374.5 and 368.5 eV are indexed to Ag(0) 3d_{3/2} and Ag(0) 3d_{5/2} of bulk silver.^[50,51] For the results of ZnO NPs/7 nm Ag and ZnO NPs/Ag NPs(annealed)/7 nm Ag, we can find that there is an obvious shift to higher binding energy for the film with Ag NPs, indicating the strong interaction between amine functional groups and Ag, as the binding energy between metal and amine groups is higher than that of pure metal.^[24] In addition, the much higher intensity of Ag 3d and extremely weaker intensity of Zn 2p (Figure S3a, Supporting Information) detected from ZnO NPs/Ag NPs/7 nm Ag exhibit the formation of a better covering ultrathin Ag film assisted by Ag NPs as compared to the case without Ag NPs (i.e., ZnO NPs/7 nm Ag), which is well consistent with the SEM results shown in Figure 2f,i. Consequently, the “ligand-optimized” Ag NPs with the 110 $^{\circ}\text{C}$ annealing for a suitable amount of maintained ligand (i.e., 53.5–57.9% oleylamine removal) on Ag NPs are obtained in the approach, and yet the temperature is the lowest in the suitable range of 110 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$ to minimize the unexpected damage on the underneath structure, particularly the organic active layer in STOSCs.

We further unveil the quality of Ag films by studying their surface morphology as the scanning electron microscope (SEM) images shown in Figure 2d–i, Figures S4 and S5 (Supporting Information). At the very early stage of evaporating Ag

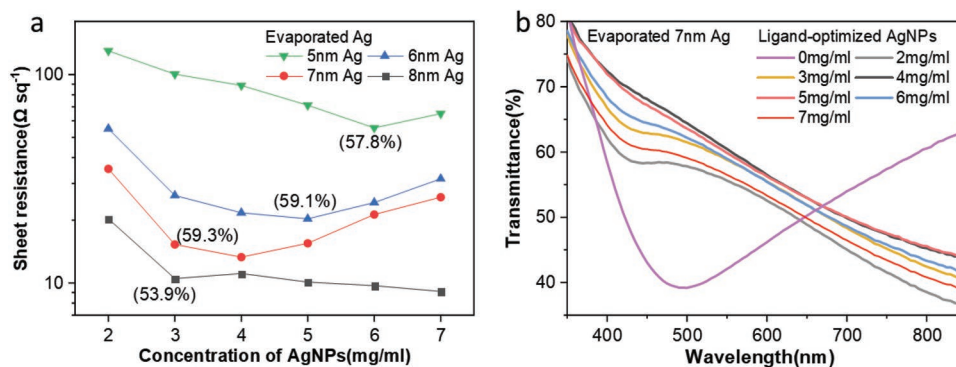


Figure 3. a) Sheet resistance of films with different concentrations of ligand-optimized AgNPs and different thicknesses of evaporated Ag, and the best AVT values for evaporated Ag thickness from 5 to 8 nm on ligand-optimized AgNPs are 57.8%, 59.1%, 59.3%, and 53.9%, as shown in parentheses. b) Transmission spectrum of evaporated 7 nm Ag on ligand-optimized AgNPs with different concentrations.

(3.5 to 5.5 nm in Figure 2d,e,g,h), the films without the ligand-optimized Ag NPs show big clusters and wide gaps between them caused by the migration and liquid-like coalescence of the evaporated Ag. Interestingly, for the case with ligand-optimized Ag, the Ag films with much denser and smaller clusters are obtained (Figure 2g,h) as compared to those with any Ag NPs, indicating that randomly pre-located and ligand-optimized Ag NPs act as anchors to guide evaporated Ag atoms for growing along remaining amine functional groups and facilitates to obtain solid-like coalescence. By continuously evaporating more Ag on Ag NPs, conductive and continuous film is achieved while big separated Ag clusters are only obtained for the Ag film without Ag NPs.

We further optimize the concentration of ligand-optimized Ag NPs ($2\text{--}7 \text{ mg mL}^{-1}$) and the amount of evaporated Ag ($5\text{--}8 \text{ nm}$) for the champion transparent electrode with low sheet resistances and best AVT as shown in Figure 3a,b. To achieve workable conductive film with higher AVT, we need to select a balanced amount of pre-located Ag NPs and the thickness of evaporated Ag. Extremely low concentrations of Ag NPs will lead to sparse density of particle distribution, which is not enough to guide the growth of evaporated Ag atoms and form the conductive film. On the other hand, extra oleylamine and denser arrangement of particles in a film deposited by the high concentration of Ag NPs will decrease the conductivity and cause a thicker film, which is not satisfactory to apply as a transparent electrode. From the results in Figure 3a, the sheet resistance of the film is strongly related to the thickness of Ag, which decreases from ≈ 100 to $\approx 10 \Omega \text{ sq}^{-1}$ while adding thickness from 5 to 8 nm. For the specific thickness of evaporated Ag ($5\text{--}7 \text{ nm}$), the sheet resistance of the film decreases first and then increases when raising the concentration of pre-located Ag NPs, thinner evaporated Ag requires relatively higher concentration of Ag NPs to obtain the lowest sheet resistance. The transmission spectra of evaporated 7 nm Ag on ligand-optimized Ag NPs with different concentrations are shown in Figure 3b, the AVT of the film increases first and then decreases when raising the concentration of pre-located Ag NPs. Consequently, our results show that the sweet spot between the concentration of Ag NPs and amount of evaporated Ag, which are 4 mg mL^{-1} and 7 nm , respectively, reveals the best-performed (champion) ultrathin Ag electrode with sheet resistance less than $15 \Omega \text{ sq}^{-1}$ and AVT of 59.3%.

Benefiting from depositing pre-located and ligand-optimized Ag NPs, the Ag NPs/Ag electrode is expected to achieve better contact with the ZnO NPs layer than the electrode without Ag NPs. Cross-section high-resolution transmission electron microscopy (TEM) on focused ion beam (FIB) processed samples is used to study the guided-growth ultrathin Ag film on devices, as shown in Figure 4. Compared with the directly deposited 7 nm Ag (Figure 4a,b) and 15 nm Ag (Figure 4d,e) samples, Ag NPs/7 nm Ag sample (Figure 4g,h) exhibits more continuous film and better interconnection with ZnO NPs layer which is consistent with our finding from SEM image (Figure 2f,i). From the high-resolution TEM images shown in Figure 4c,f, directly deposited 7 nm Ag and 15 nm Ag on ZnO NPs (without annealed Ag NPs) often exhibit mis-stacking zones in ZnO NPs layer with apparent voids around the contact interfaces (yellow highlighted regions), which ascribe to the migration of Ag clusters, the initially bonded ZnO NPs will become misplaced when the directly contacted Ag clusters merge together in the Ag film growth during the early evaporation stage. To our surprise, the better/well stacked ZnO NPs layer without any clear deformed defect zones is obtained by incorporating the ligand-optimized Ag NPs to form the ZnO NPs/Ag NPs/7 nm Ag structure (Figure 4i), indicating pre-located and ligand-optimized Ag NPs can grab and immobilize evaporated Ag clusters to suppress the occurrence of migration, which enable ultrathin film formed by guided-growth and tightly-packed small Ag clusters, as well as assist to achieve good quality ZnO NPs layer without any clear mis-stacking zones. In practical applications, Ag NPs/7 nm Ag shows better interface connection with the under layer than popularly applied 15 nm Ag (Figure S6, Supporting Information). Consequently, the above results show that the guided-growth ultrathin Ag film assisted by the ligand-optimized Ag NPs reduces the interface defects to form a high-quality transparent electrode with high AVT and good conductivity. Remarkably, the mis-stacking defect regions of the ETL can be simultaneously suppressed for improving carrier transportation collection.

2.2. High-Performance STOSCs

Using the pre-located and ligand-optimized Ag NPs (4 mg mL^{-1})/evaporated Ag (7 nm) electrode with sheet

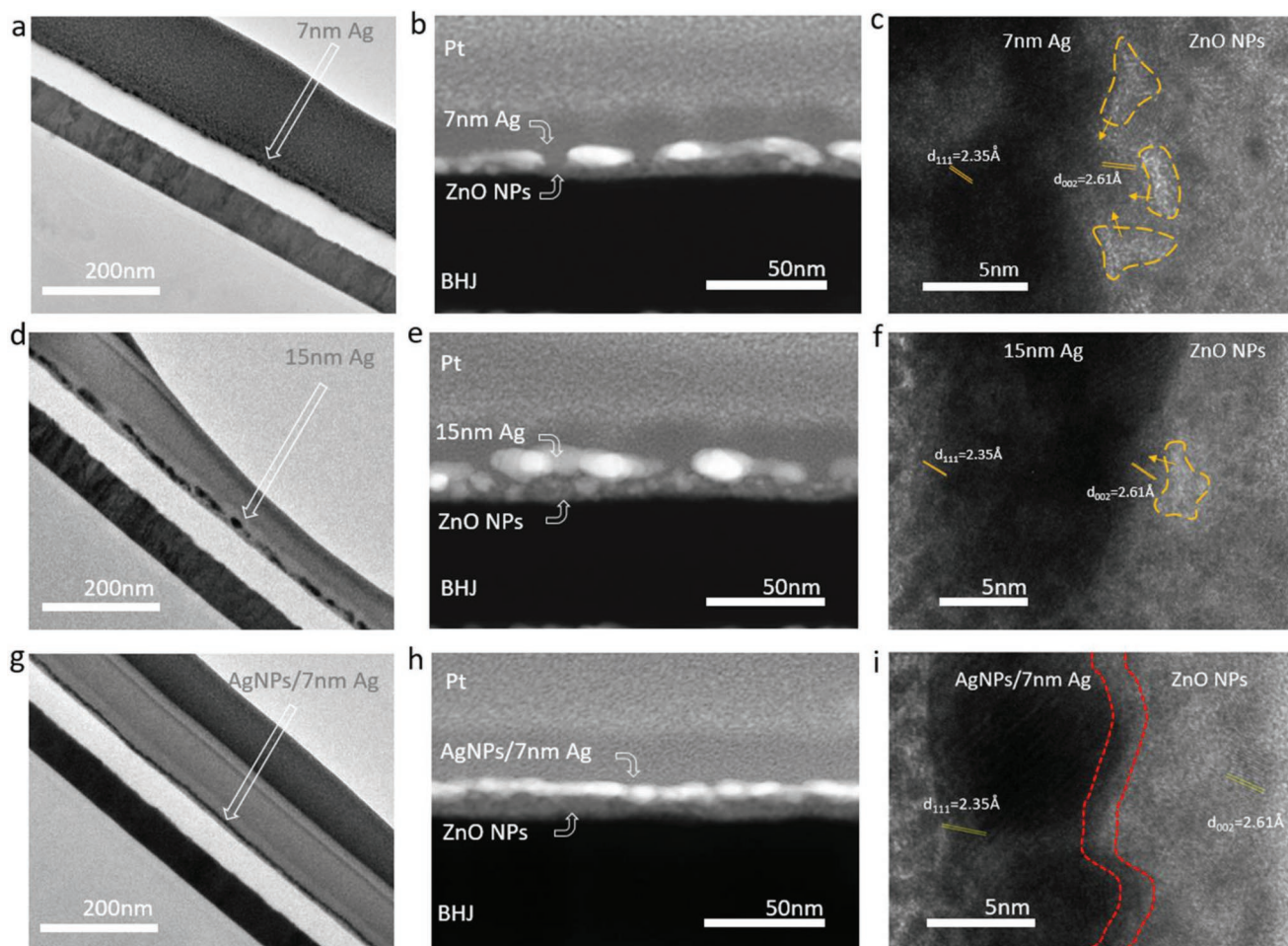


Figure 4. Cross-section TEM images of devices with a–c) evaporated 7 nm Ag, d–f) evaporated 15 nm Ag and g–i) ligand-optimized AgNPs/7 nm Ag.

resistance less than $15 \Omega \text{ sq}^{-1}$ and AVT of 59.3%, we first prepare STOSCs with a widely reported structure of glass/ITO/PEDOT:PSS/PM6:Y6(1.0:1.2, w/w)/ETL/ultrathin Ag, as shown in the inset of **Figure 5a**. STOSCs with directly evaporated 15 nm Ag as the top electrode are prepared for comparison, which has been widely reported and the devices exhibit higher LUE than STOSCs using other thicknesses of directly evaporated Ag.^[6,16,52–54] **Figure 5b** shows the top view SEM images of 15 nm Ag and Ag NPs/7 nm Ag on devices. Ag NPs/7 nm Ag exhibits more uniform coverage on ZnO NPs, which mirrors the previous TEM results. It is notable that a cleaning process as described in the device fabrication section was applied on the deposited ZnO NPs layer to achieve lower roughness for the deposition of the ultrathin electrode, as shown in **Figure S7** (Supporting Information). The representative current density-voltage (*J*-*V*) characteristics are shown in **Figure 5a** and the statistics of 20 devices are summarized in **Figure 5c**. Following the results we discussed above, there are power losses in devices with directly deposited 15 nm Ag which ascribe to lower recombination resistance caused by the leakage in electrode-ETL interface, resulting in low V_{oc} and fill factor (FF).^[55,56] Compared with STOSCs with widely used 15 nm Ag as the top electrode, devices with the optimized Ag NP/Ag electrode show lower J_{sc} of 21.26 mA cm^{-2} ascribed to the higher AVT, but higher V_{oc}

of 0.841 V and FF of 73.01%, which are close to that of opaque devices. Finally, STOSCs with PM6: Y6 as the active layer and guided-growth ultrathin Ag as the top electrode achieve PCE of 13.04% and AVT of 27.88%, exhibiting a LUE of 3.635% which is higher than that of STOSCs with 15 nm Ag, detailed *J*-*V* characteristics are shown in **Table 1**. The ETL applied in the above OSCs is ZnO NPs. To demonstrate the superiority of our strategy on guide-growth transparent top electrode, we also fabricated STOSCs with widely reported PDINO as ETL and 15 nm Ag as top electrode for comparison, detailed *J*-*V* characteristics are shown in **Table S1** (Supporting Information). The STOSCs with ZnO NPs/Ag NPs/7 nm Ag exhibit both better optical and electrical performance than devices with PDINO/15 nm Ag.

In order to understand the improved carrier extraction property of the STOSCs with the optimized Ag NPs/Ag electrodes, we study the transient photocurrent of STOSCs with same structure but different strategies on top electrodes, as shown in **Figure 5d**. A charge extraction time of 2.892 ms is obtained from the device with ligand-optimized Ag NPs/Ag electrodes, which is lower than the charge extraction time of 3.116 ms for the control device with directly evaporated 15 nm Ag, thus offering faster charge extraction. **Figure 5e** shows the electrochemical impedance spectra (EIS) results and equivalent circuit of STOSCs with a guided-growth ultrathin Ag or 15 nm Ag as

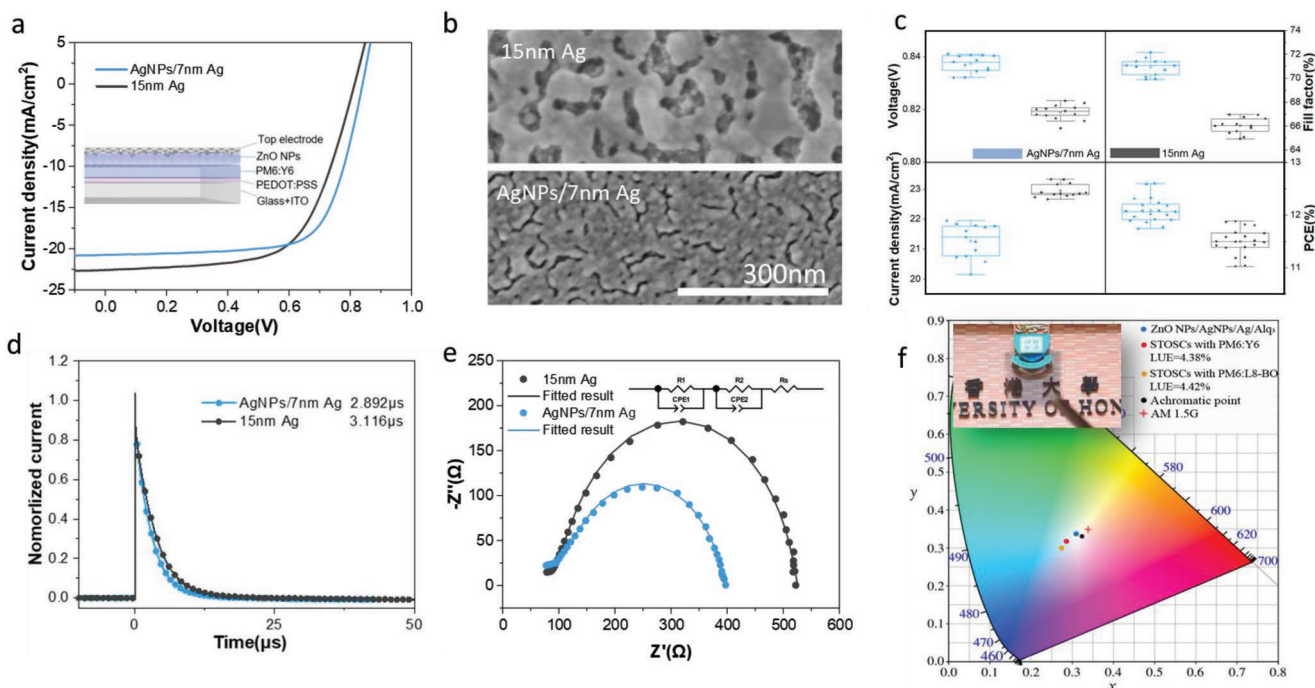


Figure 5. a) Structure and J-V curves of PM6:Y6-based STOSCs with evaporated 15 nm Ag or ligand-optimized AgNPs/7 nm Ag as top electrode. b) Top view SEM images of evaporated 15 nm Ag and ligand-optimized AgNPs/7 nm Ag on devices. c) Distribution statistics, results of d) transient photocurrent measurement and e) electrochemical impedance spectra and equivalent circuit of STOSCs with an evaporated 15 nm Ag or ligand-optimized AgNPs/7 nm Ag as top electrode. f) CIE 1931 coordinates of best-performance STOSC with PM6:L8-BO or PM6:Y6 and ZnO NPs/ligand-optimized AgNPs/7 nm Ag/Alq₃, and a photograph of best-performance PM6:L8-BO based STOSC.

the top electrode. The ESI spectra exhibit two semicircles in which R₁ indicates recombination resistance (inversely proportional to the recombination rate) and R₂ represents interlayer resistance in STOSCs.^[57] R_s and two constant phase elements (CPE1 and CPE2) were applied to present the series resistance, charge recombination capacitance, and carrier transport capacitance in STOSCs. Our results show that the device with the optimized Ag NPs/Ag electrode exhibits R₁ of 114.5 Ω and R₂ of 260 Ω, while devices with 15 nm Ag show R₁ with lower value of 84.45 Ω and R₂ with much higher value of 399 Ω. These results suggest that the interfacial contact between guided-growth ultrathin Ag and the bottom ETL is better than the one with 15 nm Ag. The detailed parameters are summarized in Table S2 (Supporting Information). All of these results confirm that the application of pre-located Ag NPs not only guides the growth of ultrathin Ag, but also provides excellent interfacial contact between the top electrode and under layer, which supports the J-V characteristics results shown in Figure 5a,c.

To realize high light utilization of semitransparent devices, a dielectric film of Tris(8-hydroxyquinoline)aluminum (Alq₃)

with an optimized thickness is deposited on ligand-optimized AgNPs/Ag to enhance the optical features of the electrode,^[58] as shown in Figure S9 (Supporting Information). The ZnO NPs/ligand-optimized AgNPs/Ag/Alq₃ structure exhibits an enhanced AVT of 75.41% while maintaining excellent electrical properties. In order to find the sweet spot between PCE and AVT, ZnO NPs/ligand-optimized AgNPs/Ag/Alq₃ structure is applied on STOSCs with different active layers. The active layer includes PM6:Y6 and PM6:L8-BO with different donor ratios for further optimization of the STOSCs. Experimental results shown in Figure 6a,d and Table 2 indicate that PM6:Y6 and PM6:L8-BO blends with low contents of PM6 can still maintain efficient charge generation and collection, and yield STOSCs with high AVT while maintaining decent efficiency. With tuning PM6:Y6 from 1:1.2 to 0.4:1.2(w/w), the efficiency of STOSCs only drops from 12.69% to 11.51%, while AVT remarkably raising from 29.30% to 38.10%, the best-performance and PM6:Y6-based STOSCs reach LUE of 4.385% with PCE of 11.51% and AVT of 38.1%. For PM6:L8-BO blends, by tuning PM6: L8-BO from 1:1.4 to 0.8:1.4(w/w), the efficiency of

Table 1. Device performance of PM6:Y6 based OSCs with different top electrodes. Average PCEs and standard deviations were obtained from 20 devices.

Top electrode	J_{sc} [mA/cm ²]	V_{oc} [V]	FF [%]	PCE [%] Best [Ave. ± Dev.]	R_s [Ω cm ²]	R_{sh} [Ω cm ²]	AVT [%]	LUE [%]
100 nm Ag	26.41	0.8410	73.97	16.42(16.15±0.11)	3.71	1285.11	—	—
15 nm Ag	22.83	0.8173	65.86	12.29(11.51±0.35)	5.75	987.56	23.31	2.865
AgNPs/7 nm Ag	21.26	0.8405	73.01	13.04(12.53±0.29)	4.12	1277.45	27.88	3.635

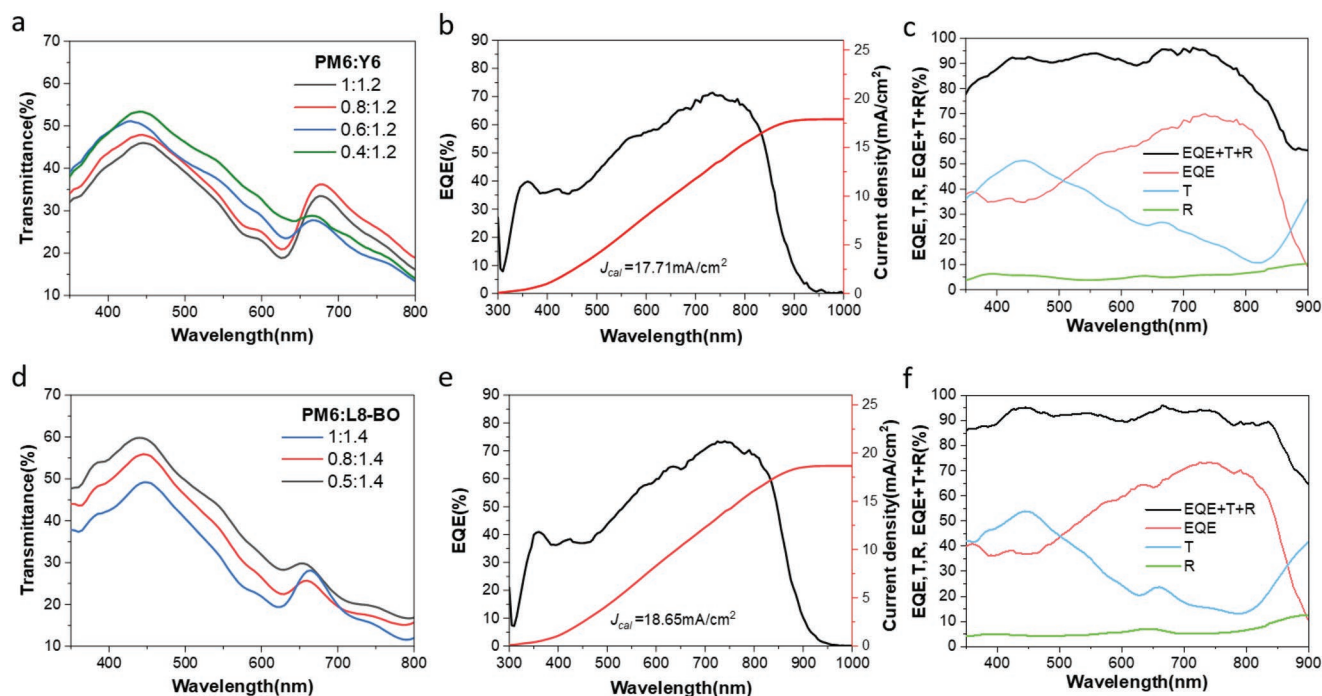


Figure 6. a) Transmission spectrum of STOSCs (ligand-optimized AgNPs/7 nm Ag/Alq₃ as top electrode) with different donor ratios in PM6:Y6. b) EQE and c) EQE+T+R of PM6:Y6 based STOSCs with highest LUE and ligand-optimized AgNPs/7 nm Ag/Alq₃ as top electrode. d) Transmission spectrum of STOSCs (ligand-optimized AgNPs/7 nm Ag/Alq₃ as top electrode) with different donor ratios in PM6:L8-BO. e) EQE and f) EQE+T+R of PM6:L8-BO based STOSCs with highest LUE and ligand-optimized AgNPs/7 nm Ag/Alq₃ as top electrode.

STOSCs drops from 13.45% to 12.80%, while AVT raising from 29.12% to 34.55%. Finally, the best PM6:L8-BO-based STOSCs achieve LUE of 4.422% with PCE of 12.80% and AVT of 34.55%, as shown Figure S10 and Table S3 (Supporting Information), which is the highest PCE reported so far in STOSCs with remarkable LUE over 4%.

To further evaluate the efficiency of STOSCs, the external quantum efficiency (EQE) and EQE+T+R of STOSCs with the highest LUE values for each active blend are determined as shown in Figure 6b,c,e,f. The color rendering index (CRI) of the guided-growth ultrathin Ag and STOSCs with the highest LUE are also investigated. The color coordinates (x, y), AVT and

Table 2. Device performance of OSCs with opaque or optimized semitransparent ligand-optimized AgNPs/7 nm Ag/Alq₃ electrode, and different donor ratios in PM6:Y6 and PM6:L8-BO. Average PCEs and standard deviations were obtained from 8 devices in parallel. O-opaque and S-semitransparent.

Active layer	Blend ratio	J_{sc} [mA/cm ²]	V_{oc} [V]	FF [%]	PCE [%] Best [Ave. $\pm$ Dev.]	AVT [%]	LUE [%]
PM6:Y6	1:1.2-O	26.41	0.8410	73.97	16.42 (16.15 $\pm$ 0.18)	—	—
	1:1.2-S	20.54	0.8403	73.55	12.69 (12.15 $\pm$ 0.33)	29.30	3.718
	0.8:1.2-O	26.12	0.8394	73.54	16.12 (15.83 $\pm$ 0.19)	—	—
	0.8:1.2-S	20.13	0.8391	73.11	12.34 (12.02 $\pm$ 0.22)	31.59	3.898
	0.6:1.2-O	25.41	0.8404	75.98	16.21 (15.92 $\pm$ 0.21)	—	—
	0.6:1.2-S	19.23	0.8388	72.88	11.75 (11.32 $\pm$ 0.23)	35.26	4.143
	0.4:1.2-O	23.73	0.8429	76.58	15.31 (15.11 $\pm$ 0.15)	—	—
	0.4:1.2-S	18.66	0.8398	73.46	11.51 (11.21 $\pm$ 0.18)	38.10	4.386
PM6:L8-BO	1:1.4-O	25.39	0.8701	78.77	17.40 (17.02 $\pm$ 0.25)	—	—
	1:1.4-S	20.33	0.8697	76.11	13.45 (13.24 $\pm$ 0.17)	29.12	3.916
	0.8:1.4-O	24.13	0.8691	77.87	16.33 (16.05 $\pm$ 0.24)	—	—
	0.8:1.4-S	19.28	0.8689	76.41	12.80 (12.38 $\pm$ 0.31)	34.55	4.422
	0.5:1.4-O	21.77	0.8671	76.55	14.45 (14.11 $\pm$ 0.24)	—	—
	0.5:1.4-S	16.56	0.8656	75.21	10.78 (10.38 $\pm$ 0.32)	39.45	4.252

CRI values from the transmission spectra of the ZnO NPs/Ag NPs/7 nm Ag/Alq₃ film and corresponding STOSCs are determined according to the method shown in SI, the wavelength range for calculation is 380–780 nm. As shown in the CIE color space presented in Figure 5f, the color coordinates of ZnO NPs/Ag NPs/Ag/Alq₃ film are located at (0.3162, 0.3440), and it is close to the achromatic point (0.33, 0.33) with calculated CRI value of 97, indicating a good neutral color sensation when looking through the film under AM1.5G illumination. Meanwhile, the corresponding best-performance devices with PM6:Y6 or PM6:L8-BO as active layer exhibit color coordinates at (0.2895, 0.3209) with CRI value of 90 and (0.2702, 0.3047) with CRI value of 87 respectively, providing a light-blue sensation to the human eye.

3. Conclusion

In summary, we demonstrate a facile approach of introducing pre-located Ag NPs with an optimized amount of ligands (with 53.5–57.9% oleylamine removal) to form high-quality and ultrathin evaporated Ag film for an efficient transparent electrode, which performs (sheet resistance < 15 Ω sq⁻¹ and AVT of 59.30%) are beyond those merely evaporated Ag electrodes. Fundamentally, with the ligand-optimized Ag NPs, we can guide the growth of the clusters of the evaporated Ag to form high-quality transparent electrode. Meanwhile, we can reduce the mis-stacking defect regions in ETL and thus favor the carrier transportation/extraction to the electrode. By using the pre-located and ligand-optimized Ag NPs/Ag/Alq₃ top electrode, the PM6:L8-BO based STOSCs achieve LUE of 4.422% while obtaining high PCE of 12.80% (the best reported PCE in STOSCs with LUE over 4%). This work contributes to not only a facile and general strategy to achieve high-quality metal-based transparent electrode, but also the detailed understanding of the formation mechanism, material and optoelectronic properties of the top electrodes for high-performance semi-transparent photonic devices.

4. Experimental Section

Materials: Silver nitrate (AgNO₃, 99%), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, 99.9%) ethanolamine (99.9%), 2-methoxyethanol (CH₃OCH₂CH₂OH, 99.8%), ethanol (99.9%), oleylamine (98%), n-octane (99%) and n-Hexane (GR) were purchased from Sigma-Aldrich. PEDOT:PSS (Baytron A14083) was purchased from H.C. Starck GmbH, Germany. PM6, Y6, L8-BO, and PDINO were purchased from Solarmer Co., Ltd. Chloroform (GR) and 1-chloronaphthalene(CN) were purchased from Sigma-Aldrich.

Silver nanoparticles (Ag NPs) were synthesized with AgNO₃ and oleylamine. Briefly, 5 mL oleylamine was preheated for 10 min at 185 °C, then 0.25 g AgNO₃ was added and the reaction was allowed for 10 min. After the reaction, Ag NPs were cleaned with ethanol four times and then dissolved in a mixed solution of n-octane and n-hexane. ZnO NPs were synthesized with ZnAc₂·2H₂O and KOH. Generally, ZnAc₂·2H₂O and KOH were first dissolved in methanol, then KOH/methanol was added in ZnAc₂·2H₂O/methanol solution drop by drop under 60 °C, then the precipitation was collected and cleaned with methanol for 3–4 times and dispersed in butanol with a concentration of 15 mg mL⁻¹.

Device Fabrication: The ITO-coated glasses were washed by sonication in ITO cleaner, deionized water, acetone, and ethanol for 15 min,

respectively. Then the substrates were treated with UV-O₃ cleaning for 20 min. For OSCs with a normal evaporated electrode, PEDOT:PSS was spin-coated on the substrate at 4000 rpm followed by 150 °C annealing for 10 min at first. Then the samples were transferred into a glove box, PM6:Y6 (with different donor-acceptor ratios in chloroform with 0.75 vol% incorporation of CN) or PM6:L8-BO (with different donor-acceptor ratios in chloroform with 0.75 vol% incorporation of CN) was dynamically spin-coated with 3000 rpm for 40 s and baked at 110 °C for 10 min. ZnO NPs (15 mg mL⁻¹) or PDINO (1 or 3 mg mL⁻¹ in methanol) was deposited on the active layer at 3000 rpm for 40 s. The devices were finished by thermal evaporating 100 or 15 nm Ag. For STOSCs with extremely thin electrode, there is no annealing after the deposition of the active layer, ZnO NPs (15 mg mL⁻¹) was directly deposited on PM6:Y6 or PM6:L8-BO film. Then Ag NPs (4 mg mL⁻¹) were dynamic spin-coated on ZnO NPs film with 2000 rpm and immediately baked at 110 °C for 10 min. The devices were finished by thermal evaporating Ag ≤ 7 nm. It is notable that an antireflection coating (ARC) of LiF/MoO₃ is integrated with a glass substrate for each semi-transparent device. All the ZnO NPs films in the above description were washed with ethanol for 5 s after deposition.

Material and Device Characterization: The morphology and elemental compositions of the electrode were analyzed using atomic force microscope (NT-MDT NTEGRA) and X-Ray spectrometer (XLESCALAB 250Xi electron spectrometer from VG Scientific with a monochromatic Al K radiation). Sheet resistance of the electrode was measured by using a four-point probe system (Keithley 2400). UV–vis absorption spectrum was measured with Shimadzu UV-Visible Spectrophotometer (UV-2600). The top and cross-section view of the ultrathin electrode were analyzed using SEM (Hitachi S-4800), FIB (FEI Quanta 200 3D), and TEM/STEM (Thermo Scientific Talos F200X). J-V curves were measured by a Keithley 2400 under solar simulator (SS-F5-3A, Enli technology Co., Ltd.). Standard silicon solar cell (SRC-2020, Enli technology Co., Ltd.) was hired to calibrate the light intensity. TPC was carried out under a 355 nm 6 ps pulse width laser. A 4 GHz Keysight MSO9404A digital oscilloscope was employed to monitor TPC signal. EIS measurement was performed on an electrochemical station (Zahner, Zennium Pro) with a frequency range from 100 Hz to 1 MHz.

Supporting Information

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

Acknowledgements

The research is supported by the seed funds (Grant Nos. 202011159254 and 202111159113), from the University Grant Council of the University of Hong Kong, the General Research Fund (Grant Nos. 17200518, 17201819, 17211220 and 17200021), Collaborative Research Fund (Grant No. C7035-20G and C5037-18G) from Hong Kong Special Administrative Region, China, and the support from Innovation and Technology Fund (MRP/040/21X and ITS/277121FP). It is also supported by the Shenzhen Science, Technology and Innovation Commission (JCYJ20220530113014033), the Department of Education of Guangdong Province University Innovation Foundation (2021KTSCX107), and the National Natural Science Foundation of China (Grant No. 62150610496).

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

facile formation approach, organic solar cells, semi-transparent devices, ultrathin metal films

Received: September 27, 2022

Revised: November 15, 2022

Published online:

- [1] A. Polman, M. Knight, E. C. Garnett, B. Ehrler, W. C. Sinke, *Science* **2016**, 352, 6283.
- [2] V. V. Brus, J. Lee, B. R. Luginbuhl, S.-J. Ko, G. C. Bazan, T.-Q. Nguyen, *Adv. Mater.* **2019**, 31.
- [3] M. Zhang, L. Zhu, G. Zhou, T. Hao, C. Qiu, Z. Zhao, Q. Hu, B. W. Larson, H. Zhu, Z. Ma, *Nat. Commun.* **2021**, 12, 309.
- [4] L. Zhu, M. Zhang, J. Xu, C. Li, J. Yan, G. Zhou, W. Zhong, T. Hao, J. Song, X. Xue, *Nat. Mater.* **2022**, 21, 656.
- [5] Y. Xie, L. Huo, B. Fan, H. Fu, Y. Cai, L. Zhang, Z. Li, Y. Wang, W. Ma, Y. Chen, Y. Sun, *Adv. Funct. Mater.* **2018**, 28, 1800627.
- [6] P. Yin, Z. Yin, Y. Ma, Q. Zheng, *Energy Environ. Sci.* **2020**, 13, 5177.
- [7] Y. Zhang, D. Luo, C. Shan, Q. Liu, X. Gu, W. Li, W. C. H. Choy, A. K. K. Kyaw, *Sol. RRL* **2022**, 6, 2100785.
- [8] C. Xu, K. Jin, Z. Xiao, Z. Zhao, X. Ma, X. Wang, J. Li, W. Xu, S. Zhang, L. Ding, F. Zhang, *Adv. Funct. Mater.* **2021**, 31, 2107934.
- [9] Y. Xie, Y. Cai, L. Zhu, R. Xia, L. Ye, X. Feng, H.-L. Yip, F. Liu, G. Lu, S. Tan, Y. Sun, *Adv. Funct. Mater.* **2020**, 30, 2002181.
- [10] Z. Hu, J. Wang, X. Ma, J. Gao, C. Xu, X. Wang, X. Zhang, Z. Wang, F. Zhang, *J. Mater. Chem. A* **2021**, 9, 6797.
- [11] C. Xu, K. Jin, Z. Xiao, Z. Zhao, Y. Yan, X. Zhu, X. Li, Z. Zhou, S. Y. Jeong, L. Ding, H. Y. Woo, G. Yuan, F. Zhang, *Sol. RRL* **2022**, 6, 2200308.
- [12] Z. Hu, Z. Wang, Q. An, F. Zhang, *Sci. Bull.* **2020**, 65, 131.
- [13] Z. Hu, J. Wang, Z. Wang, W. Gao, Q. An, M. Zhang, X. Ma, J. Wang, J. Miao, C. Yang, F. Zhang, *Nano Energy* **2019**, 55, 424.
- [14] T. Li, S. Dai, Z. Ke, L. Yang, J. Wang, C. Yan, W. Ma, X. Zhan, *Adv. Mater.* **2018**, 30, 1705969.
- [15] Y. Chang, X. Zhu, L. Zhu, Y. Wang, C. Yang, X. Gu, Y. Zhang, J. Zhang, K. Lu, X. Sun, Z. Wei, *Nano Energy* **2021**, 86, 106098.
- [16] D. Wang, R. Qin, G. Zhou, X. Li, R. Xia, Y. Li, L. Zhan, H. Zhu, X. Lu, H.-L. Yip, H. Chen, C.-Z. Li, *Adv. Mater.* **2020**, 32, 2001621.
- [17] Y. Wang, B. Jia, F. Qin, Y. Wu, W. Meng, S. Dai, Y. Zhou, X. Zhan, *Polymer* **2016**, 107, 108.
- [18] L. Bu, Z. Liu, M. Zhang, W. Li, A. Zhu, F. Cai, Z. Zhao, Y. Zhou, *ACS Appl. Mater. Interfaces* **2015**, 7, 17776.
- [19] J. Czolk, A. Puetz, D. Kutsarov, M. Reinhard, U. Lemmer, A. Colmann, *Adv. Energy Mater.* **2013**, 3, 386.
- [20] F. Guo, X. Zhu, K. Forberich, J. Krantz, T. Stubhan, M. Salinas, M. Halik, S. Spallek, B. Butz, E. Spiecker, T. Ameri, N. Li, P. Kubis, D. M. Guldi, G. J. Matt, C. J. Brabec, *Adv. Energy Mater.* **2013**, 3, 1062.
- [21] G. Ji, Y. Wang, Q. Luo, K. Han, M. Xie, L. Zhang, N. Wu, J. Lin, S. Xiao, Y.-Q. Li, L.-Q. Luo, C.-Q. Ma, *ACS Appl. Mater. Interfaces* **2018**, 10, 943.
- [22] Y. S. Fang, Z. C. Wu, J. Li, F. Y. Jiang, K. Zhang, Y. L. Zhang, Y. H. Zhou, J. Zhou, B. Hu, *Adv. Funct. Mater.* **2018**, 28, 8.
- [23] M. L. Xie, H. Lu, L. P. Zhang, J. Wang, Q. Luo, J. Lin, L. X. Ba, H. Liu, W. Z. Shen, L. Y. Shi, C. Q. Ma, *Sol. RRL* **2018**, 2, 10.
- [24] Y. Zhang, X. He, D. Babu, W. Li, X. Gu, C. Shan, A. K. K. Kyaw, W. C. H. Choy, *Adv. Opt. Mater.* **2021**, 9, 2002108.
- [25] X. He, Y. Wang, H. Lu, D. Ouyang, Z. Huang, W. C. H. Choy, *J. Mater. Chem. A* **2020**, 8, 6083.
- [26] J. H. Heo, D. H. Shin, D. H. Song, D. H. Kim, S. J. Lee, S. H. Im, *J. Mater. Chem. A* **2018**, 6, 8251.
- [27] D. H. Shin, C. W. Jang, H. S. Lee, S. W. Seo, S.-H. Choi, *ACS Appl. Mater. Interfaces* **2018**, 10, 3596.
- [28] Y. Song, S. Chang, S. Gradecak, J. Kong, *Adv. Energy Mater.* **2016**, 6, 1600847.
- [29] P. You, Z. Liu, Q. Tai, S. Liu, F. Yan, *Adv. Mater.* **2015**, 27, 3632.
- [30] Y. Zhou, X. Yin, Q. Luo, X. Zhao, D. Zhou, J. Han, F. Hao, M. Tai, J. Li, P. Liu, K. Jiang, H. Lin, *ACS Appl. Mater. Interfaces* **2018**, 10, 31384.
- [31] F. R. Li, Y. Xu, W. Chen, S. H. Xie, J. Y. Li, *J. Mater. Chem. A* **2017**, 5, 10374.
- [32] I. Jeon, J. Yoon, U. Kim, C. Lee, R. Xiang, A. Shawky, J. Xi, J. Byeon, H. M. Lee, M. Choi, S. Maruyama, Y. Matsuo, *Adv. Energy Mater.* **2019**, 9, 10.
- [33] I. Jeon, C. Delacou, A. Kaskela, E. I. Kauppinen, S. Maruyama, Y. Matsuo, *Sci. Rep.* **2016**, 6, 1.
- [34] J. Yun, *Adv. Funct. Mater.* **2017**, 27, 1606641.
- [35] N. Kaiser, *Appl. Opt.* **2002**, 41, 3053.
- [36] M. Henzler, T. Lüer, A. Burdach, *Phys. Rev. B* **1998**, 58, 10046.
- [37] J. Meiss, M. Riede, K. Leo, *Appl. Phys. Lett.* **2009**, 94, 013303.
- [38] M. B. Upama, M. Wright, N. K. Elumalai, M. A. Mahmud, D. Wang, C. Xu, A. Uddin, *ACS Photonics* **2017**, 4, 2327.
- [39] D. Han, H. Kim, S. Lee, M. Seo, S. Yoo, *Opt. Express* **2010**, 18, A513.
- [40] S. Lim, D. Han, H. Kim, S. Lee, S. Yoo, *Sol. Energy Mater. Sol. Cells* **2012**, 101, 170.
- [41] L. Ke, S. C. Lai, H. Liu, C. K. N. Peh, B. Wang, J. H. Teng, *ACS Appl. Mater. Interfaces* **2012**, 4, 1247.
- [42] H. Shi, R. Xia, C. Sun, J. Xiao, Z. Wu, F. Huang, H.-L. Yip, Y. Cao, *Adv. Energy Mater.* **2017**, 7, 1701121.
- [43] C.-C. Chueh, S.-C. Chien, H.-L. Yip, J. F. Salinas, C.-Z. Li, K.-S. Chen, F.-C. Chen, W.-C. Chen, A. K.-Y. Jen, *Adv. Energy Mater.* **2013**, 3, 417.
- [44] X. He, Y. Wang, L. Zhang, R. Zhang, J. Kim, K. S. Wong, Y. Chen, W. C. H. Choy, *Adv. Funct. Mater.* **2021**, 31, 2010764.
- [45] G. Xue, Q. Dai, S. Jiang, *J. Am. Chem. Soc.* **1988**, 110, 2393.
- [46] Y. Zhou, R. Ma, Y. Ebina, K. Takada, T. Sasaki, *Chem. Mater.* **2006**, 18, 1235.
- [47] H. Kang, S. Jung, S. Jeong, G. Kim, K. Lee, *Nat. Commun.* **2015**, 6, <https://doi.org/10.1038/ncomms8373>.
- [48] F. Gao, Z. Gu, in *Handbook of Nanoparticles*, Springer, Switzerland **2016**, p. 661.
- [49] S. Mourdikoudis, L. M. Liz-Marzán, *Chem. Mater.* **2013**, 25, 1465.
- [50] I. Lopez-Salido, D. C. Lim, Y. D. Kim, *Surf. Sci.* **2005**, 588, 6.
- [51] S. W. Han, Y. Kim, K. Kim, *J. Colloid Interface Sci.* **1998**, 208, 272.
- [52] W. Liu, S. Sun, S. Xu, H. Zhang, Y. Zheng, Z. Wei, X. Zhu, *Adv. Mater.* **2022**, 34, 2200337.
- [53] Y. Li, J.-D. Lin, X. Che, Y. Qu, F. Liu, L.-S. Liao, S. R. Forrest, *J. Am. Chem. Soc.* **2017**, 139, 17114.
- [54] Z.-P. Yu, X. Li, C. He, D. Wang, R. Qin, G. Zhou, Z.-X. Liu, T. R. Andersen, H. Zhu, H. Chen, *Chin. Chem. Lett.* **2020**, 31, 1991.
- [55] C. M. Proctor, T.-Q. Nguyen, *Appl. Phys. Lett.* **2015**, 106, 083301.
- [56] B. Mazhari, *Sol. Energy Mater. Sol. Cells* **2006**, 90, 1021.
- [57] A. Pockett, H. K. H. Lee, B. L. Coles, W. C. Tsoi, M. J. Carnie, *Nanoscale* **2019**, 11, 10872.
- [58] X. Ren, X. Li, W. C. H. Choy, *Nano Energy* **2015**, 17, 187.