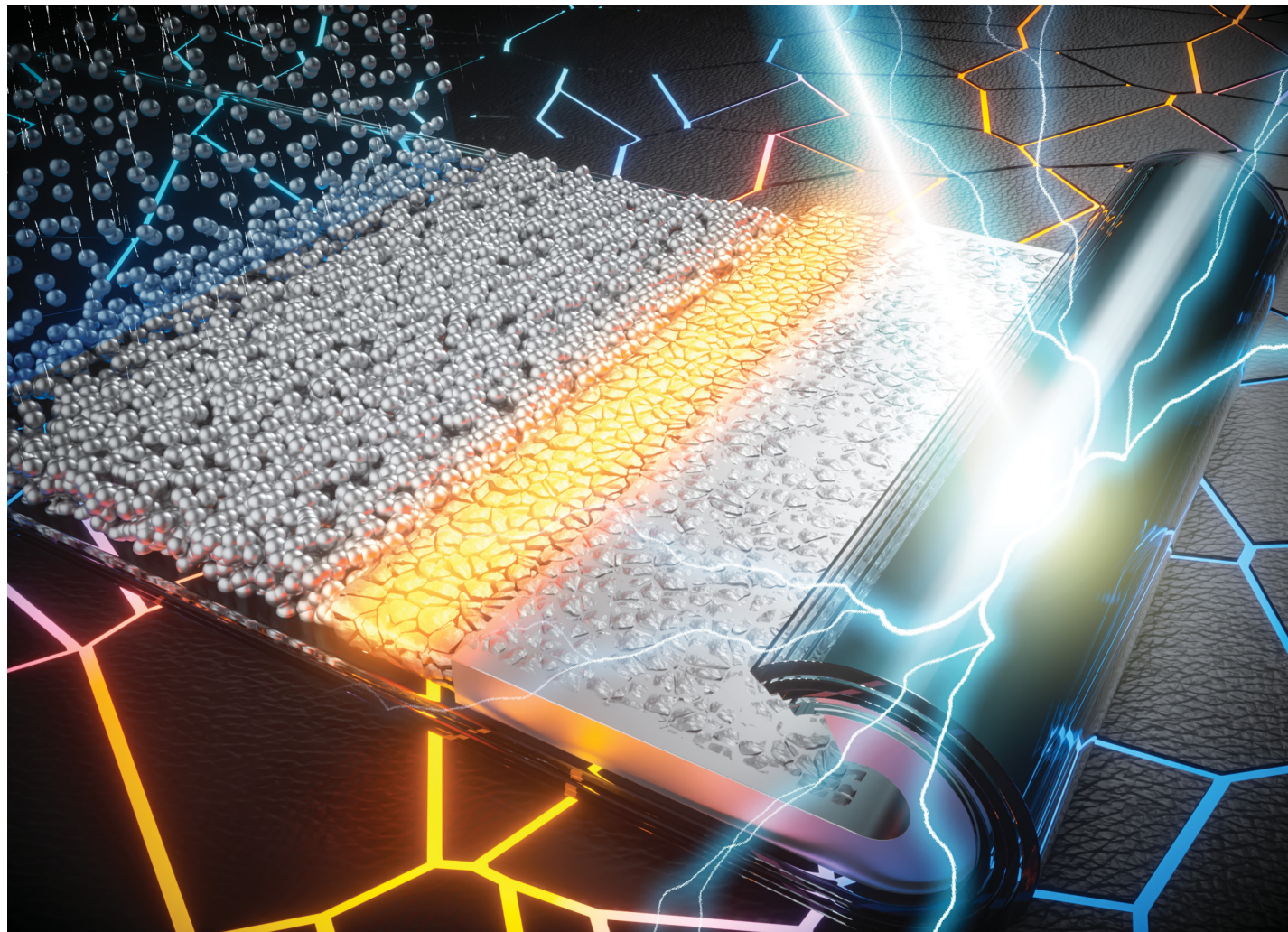




Showcasing research from Professor Wallace Choy's laboratory, University of Hong Kong, Hong Kong, China.

A bottom-up understanding of the ligand-dominated formation of metallic nanoparticle electrodes with high broadband reflectance for enabling fully solution-processed large-area organic solar cells

Choy's team demonstrate a compact-packing approach for stacking and sintering metallic nanoparticles for top electrodes with high conductivity and high broadband reflectance for high-throughput large-scale applications. Featuring the self-packing ability of silver nanoparticles (AgNPs) and superior space proportion of silver, gallic-acid-assisted AgNPs with a uniform distribution of particle size and superior storage stability from high-quality AgNP film in low-temperature sintering enabling fully solution-processed large-area organic solar cells with the record efficiency of 14.69%.

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A bottom-up understanding of the ligand-dominated formation of metallic nanoparticle electrodes with high broadband reflectance for enabling fully solution-processed large-area organic solar cells†

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Solution-processed top electrodes using metallic nanoparticles have great potential in the high-throughput large-scale industrialization of organic solar cells (OSCs). To overcome poor reflectance, severe conditions of post-treatments, and unclear bottom-up formation mechanisms from nanoscale materials to bulk electrode films, we propose a compact-packing-enabled fabrication approach for stacking and then sintering metallic nanoparticles to become very efficient top electrodes with high conductivity and high broadband reflectance. We establish the formation mechanism in which spray-coated silver nanoparticle (AgNP) electrodes ligated by gallic acid (GA) form well-dispersed compactly packed structures during the stacking. Featuring the self-packing ability of AgNPs and a much higher space proportion of silver, GA-assisted AgNPs with a uniform distribution of particle size and superior storage stability form high-quality AgNP films in low-temperature sintering. Finally, attributing to the superior electrical and optical properties, and facile post-treatment of electrodes, the fully solution-processed OSCs with the GA-assisted AgNP electrodes achieve a record high efficiency of 14.69% for large-area devices ($\geq 1 \text{ cm}^2$).

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Broader context

Highly reflective electrodes are an important component in optoelectronic applications, such as photovoltaics, light-emitting diodes, and detectors. In general, most of the reported devices will form rear electrodes by vapor deposition methods, such as thermal evaporation or magnetron sputtering, owing to their homogeneous and compact properties. Nevertheless, those methods inevitably require tremendous energy consumption and are incompatible with high-throughput and large-area fabrication. Differently, solution-processed top electrodes (STEs) including silver nanoparticle (AgNP) based STEs with interesting features of a cost-effective and easy fabrication process can be potential candidates. However, it is challenging to fabricate good AgNP electrodes because of their poor reflectance, severe conditions of post-treatment, and unclear bottom-up formation mechanisms from nanoscale materials to bulk electrode films. In this work, we elaborate on the bottom-up formation process of AgNPs with different ligands and build up the guideline of ligand selection for nanoparticles not only for electrodes but also for the assembled or stacked particles in other contexts such as bio-science. By using a selected ligand of gallic acid (GA), we realize a self-assembly-enabled fabrication approach for stacking and then sintering metallic nanoparticles to become very effective top electrodes with high conductivity and high broadband reflectance offering excellent electrical and optical properties of AgNP STEs. Finally, fully solution-processed OSCs with the GA-based AgNP STEs achieved a record high efficiency in large-area OSCs.

Introduction

Organic solar cells (OSCs) have attracted much attention in the past decades because of their lightweight, flexibility, low cost, and simple fabrication process.^{1–5} To date, the power conversion efficiency (PCE) of OSCs has reached over 19% for single junction cells^{6–8} and over 20% for tandem cells.⁹ To promote the industrialization of OSCs, large-area devices are highly

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desirable. However, large-area devices have much more complex and exacting requirements, such as material restriction,^{10,11} deposition methods,^{12,13} and layer thickness of multi-layered device structures.^{14,15} Much effort has been contributed to the large-area OSCs and satisfactory efficiency has been achieved.^{14,15} In general, most of the reports selected the rear electrodes formed by vapor deposition methods, such as thermal evaporation or magnetron sputtering, owing to their homogeneous and compact properties. Zangwill and colleagues illustrated the general deposition process of these solid films, in which the growth and erosion affect the film deposition synergistically.¹⁶ The morphological evolution of the thin film growth and smoothing was demonstrated, pointing out the fundamental depositing procedure of ultrasmall components. Nevertheless, thermal evaporation and magnetron sputtering inevitably consume a tremendous amount of energy and are incompatible with high-throughput and large-area manufacturing. Differently, solution-processed top electrodes (STEs) with interesting features of a cost-effective and easy fabrication process can be potential candidates for promoting large-area OSCs. Regrettably, the reported all-solution processed large-area OSCs presented relatively low efficiency, suffering from unsatisfactory conductivity and reflectance of STEs.

Silver nanoparticles (AgNPs) are a potential candidate for high-quality reflective electrodes owing to their high conductivity and reflectance of their bulk material. In general, the formation of AgNP conductive films involves two steps: particle deposition and sintering, in which the ligands on the particles may significantly influence the stacking conditions and sintering process, resulting in a complex packing structure and harsh sintering requirements. Many researchers have investigated the assembly of nanoparticles with different ligands. A rigid core with a soft ligand shell can assemble into a phase characteristic of dense packing and internal surface area minimization, while the length of ligands can determine the packing model of particles between hard and soft balls.¹⁷ In addition, the selection of suitable ligands can manipulate not only the particle shape and size¹⁸ but also the assembled superlattices,¹⁹ which can significantly affect the packing methods of particles and film qualities.^{20–22} These assembled structures offer excellent opportunities for the subsequent conductive thin film formation, after interparticle tunneling or removing organic ligands. For instance, citrate-covered particles are demonstrated to form assembled particle islands, resulting in a suppressed tunneling barrier and a film's conductivity of over 4000 S cm^{-1} , while other ligands restrain the electron transport of films due to the large interparticle distance.²³ Furthermore, many researchers have demonstrated that ligands can be split away from the silver surface after photonic,^{24,25} chemical,²⁶ plasma,²⁷ or thermal²⁸ treatments, contributing to interparticle contact and realizing decent conductivities of sintered particles. However, few reported methods can remove the ligands from the particles in films and transform the 'stacked particles' structure to uniform film under a soft post-treatment, which is highly desirable for electronic applications. Consequently, the remaining insulating ligands and the spherical shape of particles in the sintered thin films severely limit the film quality and subsequently the optical and electrical properties.

The nano-size Ag particles absorb and scatter light extraordinarily because of the collective oscillation of surface electrons, known as surface plasmon resonance (SPR).^{29–32} More ligands remaining in the AgNP film may make it harder to lose the 'stacked particles' structure, contributing to more potent SPR effects. Compared with commonly used evaporated or sputtered silver electrodes, AgNP thin films may suffer a significant loss of current density in photovoltaic applications. As a result, few reported works demonstrated high-quality reflective electrodes based on solution-processed AgNPs.

Herein, we elaborate on the fundamentals of depositing and sintering AgNPs with different ligands, proposing a strategy to select the ideal ligand for AgNPs accordingly, which realizes high stacking density AgNP films with superior electrical and optical properties after sintering at a low temperature. Gallic acid (GA), as a selected candidate, performs as a reductant and stabilized ligand for AgNP synthesis. The short-chain molecular structure and multiple interactions with AgNPs benefit the high space proportion of silver in particles and compact packing during deposition, contributing to a tightly stacked AgNP thin film with a higher density of silver compared to AgNP films with other ligands. Furthermore, unlike commonly-used ligands, GA can decompose at low temperatures and release from the AgNP films, contributing to a facile sintering process for AgNPs and producing a relatively pure silver film. As a result, the AgNP electrodes can show a low sheet resistance of $1.6 \Omega \text{ sq}^{-1}$ and a high average reflectance of 92% with a thickness of around 300 nm. Benefiting from the superior electrical and optical properties of the AgNP electrodes, evaporation-free OSCs exhibit a record PCE of 14.69% for a large-area device (1 cm^2), outperforming other fully solution-processed large-area OSCs.

Results and discussion

The commonly used STE materials are conductive polymers, carbon-based nanomaterials, and metal-based materials. The most famous conductive polymer for the solution-processed electrode is the PEDOT:PSS, which shows good conductivity after treatments and great flexibility.^{33,34} Nevertheless, the intense light absorbance induced by the nature of the material limits its potential for performing as reflective electrodes. The serious wetting problems also make it hard to be deposited on the top of OSCs.³⁵ Carbon-based materials, including carbon nanotubes (CNT, 1D) and graphene (2D), also suffer from similar problems and find it difficult to perform as ideal reflective electrodes. Moreover, the poor inter-piece or inter-tube contact significantly increases the resistance of the electrodes.^{36–38} Metal-based materials such as Ag nanowires (AgNWs), Ag micro-particles or -plates inks, and AgNPs have been intensively investigated because of their high conductivity in bulk materials. AgNWs are widely used as transparent conductive electrodes (TCEs) because of their high figure of merit (FoM) of TCEs and their easy fabrication process.^{39,40} However, AgNWs cannot perform as reflective electrodes due to the low coverage ratio of the network structure. Commercial Ag inks usually contain various

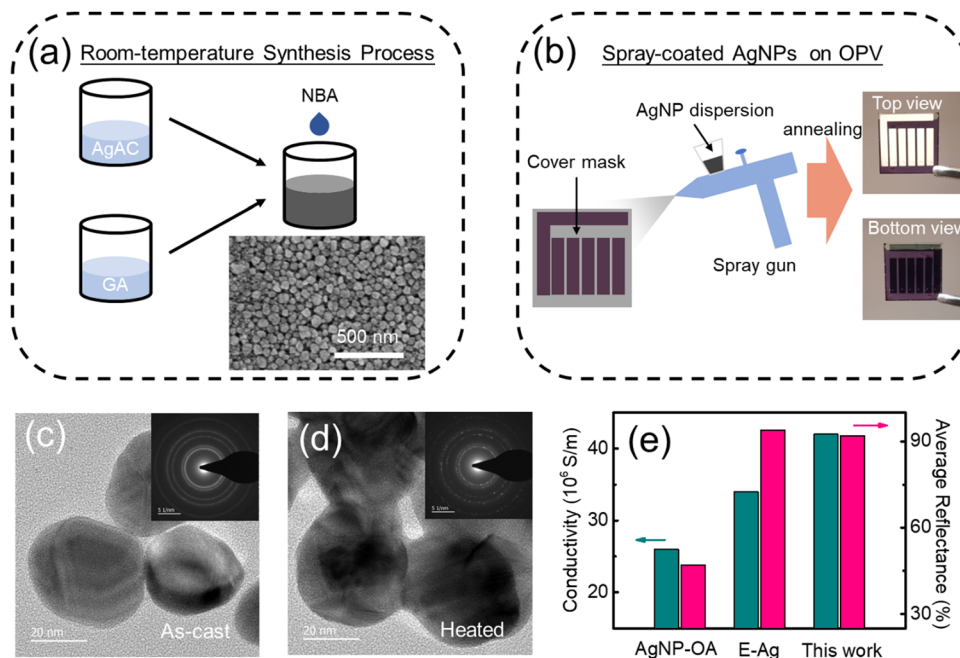


Fig. 1 (a) The schematic diagram of the room-temperature synthesis process of silver nanoparticles; the inset image is the SEM image of AgNPs. (b) The schematic diagram of spray coating AgNPs. A patterned cover mask introduces the pattern of rear electrodes. The inset photographs are the top and bottom views of an actual OSC with a spray-coated AgNP electrode. (c and d) TEM images of AgNPs before and after annealing with a scale bar of 20 nm. The inset images are the corresponding electron diffraction patterns with a scale bar of 5 1/nm. (e) The comparison of conductivities and average reflectance (400–900 nm) of three electrodes: a commonly-reported sintered AgNPs with oleyamine as ligands (AgNP-OA), evaporated silver (E-Ag), and the sintered AgNPs assisted with gallic acid (this work).

additives which may increase the penetration risk during the solution process.²⁶ In addition, the micron-size Ag components in the inks make it hard to fabricate uniform films and ideal interfaces with the underlying layer.^{41,42} Thus, the silver nanoparticle is a potential candidate for STE application because of its high conductivity and reflectance of the bulk material and high coverage of the film formation.

There are two steps to realize solution-processed top electrodes with AgNPs: (1) synthesizing AgNPs with opportune ligands to achieve ideal particle size and dispersity in the solvent; (2) depositing the AgNP thin film on a target substrate and sintering the AgNPs to make the film conductive. Fig. 1a presents the facile synthesis process of AgNPs assisted with GA in this work. *N*-Butylamine (NBA) is selected as the catalyst because of its low boiling point. The inset scanning electron microscope (SEM) image exhibits the morphology of the optimized particles. A detailed discussion on the synthesis process and characteristics of AgNPs can be found in the ESI.[†] Notably, the GA-assisted AgNPs present a uniform distribution of particle size and superior storage stability, which is compatible with commercial applications. Performing as the solution-processed top electrodes on OSCs, AgNPs should be coated gently on the top of the device with few influences on the underneath layers. Spin-coating, blade-coating, spray-coating, and slot-casting are commonly used methods for solution-processed deposition.⁴³ Compared to other methods, spray-coating deposition is least affected by the solvents due to the rapid evaporation of microdroplets.⁴⁴ Therefore, the AgNP electrodes are fabricated by spray coating with a portable

spray gun, as shown in Fig. 1b. A cover mask is employed during spray-coating to introduce the expected patterns. The top and bottom views of an actual OSC with a spray-coated electrode are also exhibited in Fig. 1b, demonstrating no visible damage after AgNPs deposition.

Moreover, the fresh AgNP electrodes are barely conductive because of the insulating ligands between particles. Typically, the thermal sintering process for AgNP electrodes is conducted at over 200 °C, which is incompatible with OSC manufacture. On the other hand, this work uses a low-temperature sintering process to improve the conductivity of AgNP films. The TEM images of AgNPs before and after annealing are conducted to verify the sintering process, as shown in Fig. 1c and d. The corresponding electron diffraction patterns are also shown in the inset images. It can be found that, before the annealing process, the boundaries between AgNPs are clear. After annealing, the boundaries disappear, indicating interparticle contact, which promotes the film's conductivity. In the electron diffraction patterns, the diffraction rings of Ag present a polycrystalline structure, which is rational to AgNPs. In contrast, the annealed AgNPs show the same rings with some conspicuous spots, indicating that the Ag-based film generates some strong lattice orientations in the polycrystalline structure. This result is consistent with the TEM images. The large-scale TEM images are demonstrated in Fig. S4 (ESI[†]). Similarly, the boundaries are clear; even the particles are stacked. After annealing, the particles sintered, contributing to larger particles. As a result, the annealed AgNP electrodes achieve high conductivity. Unlike other reported

AgNP electrodes, GA-assisted AgNP electrodes present simultaneously higher conductivity and reflectance. A widely reported AgNP synthesized with common oleylamine (AgNP-OA), and an evaporated silver (E-Ag) film is used for comparison in Fig. 1e. The conductivities and average reflectances (400–900 nm), which are the most critical characteristics of rear electrodes, present as $26 \times 10^6 \text{ S m}^{-1}$ and 47% for AgNP-OA, $34 \times 10^6 \text{ S m}^{-1}$ and 94% for evaporated Ag, and $42 \times 10^6 \text{ S m}^{-1}$ and 92% for GA-assisted AgNP electrodes. The GA-assisted AgNPs show the best performance among all solution-processed rear electrodes to our best knowledge, comparable to evaporated ones and much higher than the AgNP-OA. In a word, GA-assisted AgNPs present great potential as a rear electrode due to its superior electrical and optical properties.

Although the AgNP-GA thin films exhibit a great performance of conductivity and reflectance, the fundamental mechanism to realize high-quality particle-related electrodes is not clear yet. Thus, a comprehensive elaboration on thin film formation with metallic nanoparticles is demonstrated in Fig. 2. To declare the

outstanding role of ligands in film formation, GA and OA are chosen as candidates due to their different chemical characteristics, which will be discussed in detail in the following content. During the bottom-up formation process from nanoparticles to bulk films, the organic ligands significantly influence the film quality in several aspects. Firstly, the molecular structure and chain length of ligands determine the microscopic morphology of AgNPs. GA and OA, which have different molecular structures and carbon chain lengths (shown in Fig. 2a and d), are employed as the stabilizing ligands of AgNPs. Fig. 2b and c display the schematic diagram of two contacted GA-covered and OA-covered AgNPs. GA has a compact molecular structure and several functional groups which can interact with AgNP, while OA contains only one functional group, which can interact with Ag, and a long carbon chain tail. As a result, the AgNP-GA and AgNP-OA can be recognized as ‘hard’ and ‘soft’ spheres, respectively, during the stacking of particles. Moreover, because of the steric hindrance, there are always outward-facing functional groups of GA, which may interact with neighborhood particles,

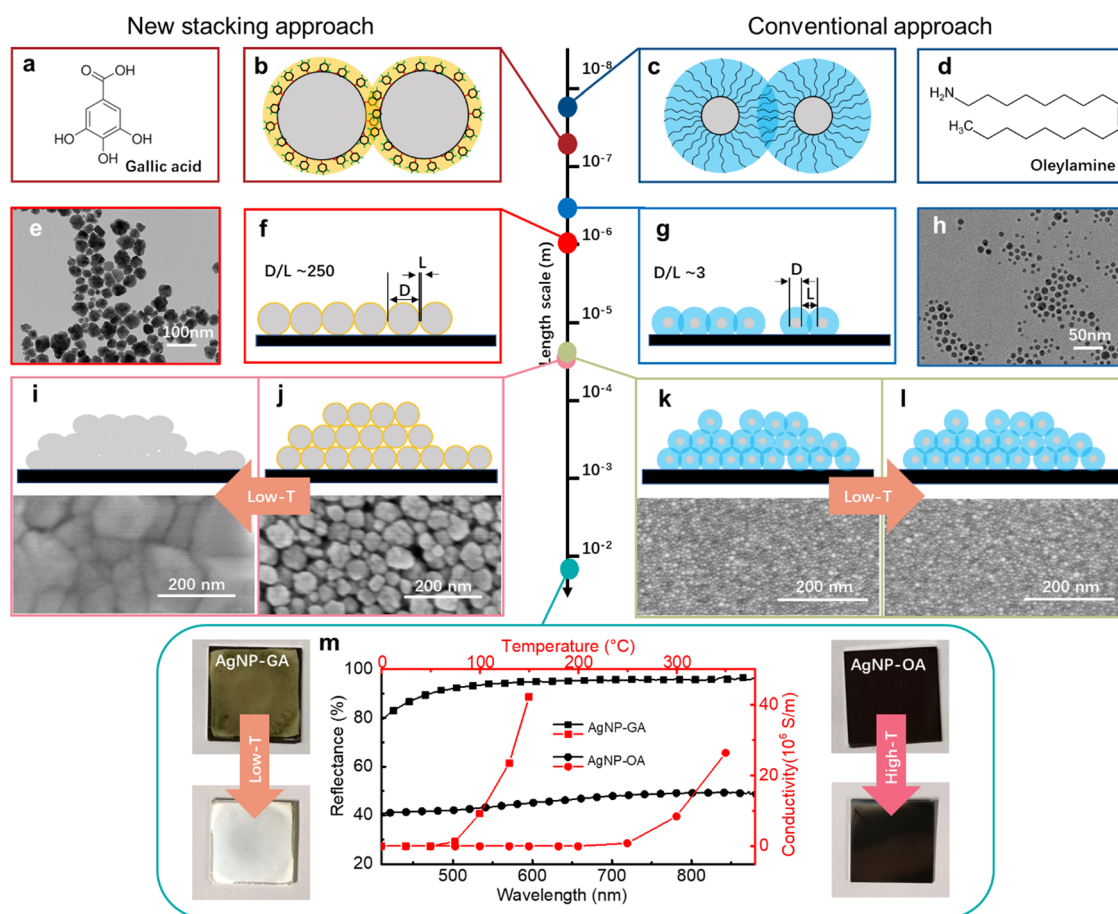


Fig. 2 Thin film formation with silver nanoparticles with different ligands, shown across orders of magnitude on the length scale. (a–d) The molecular structure of (a) GA and (d) OA. The schematic diagrams of two contacted AgNPs with (b) GA and (c) OA as ligands. (f and g) The schematic diagrams and (e and h) TEM images of the one-layer distribution of AgNPs with GA and OA ligands. The schematic diagrams of (j and k) stacking and (i and l) sintering process at a low temperature of AgNPs with GA and OA ligands. The following SEM images are stacked AgNPs before and after low-temperature annealing. (m) The reflectance spectrum and the conductivities-temperature curves of centimeter-level AgNP thin films. The photograph of AgNP-GA and AgNP-OA films before and after thermal sintering for 10 min. The annealing temperature is 100 °C for AgNP-GA and 250 °C for AgNP-OA, respectively.

benefiting the electrostatic adherence ability of AgNP-GA. On the contrary, the long carbon chain tails of OA will prevent the interaction between particles. The schematic diagrams of the particle assembly of AgNP-GA and AgNP-OA are shown in Fig. 2f and g. It can be observed that the adherence ability of AgNP-GA contributes to a compactly contacted cluster of particles, while AgNP-OA seems relatively loose. The TEM images of two types of AgNPs are exhibited in Fig. 2e and h and show consistent particle distribution with the previous statements. In addition, the space proportion of silver (Ag_{sp}) is significantly influenced by the particle structure. The ratios of the diameter of the silver sphere (D) to the length between spheres (L) are $D/L = \sim 250$ of AgNP-GA and $D/L = \sim 3$ of AgNP-OA (these values are derived from the Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) results, shown in Fig. S5 and S6, ESI† in detail) indicating that the AgNP-GA thin film can achieve a much higher space proportion of silver compared to AgNP-OA. We assume that the particles were uniform and stacked in hexagonal close packing. The average density of particles, including metal and ligands, is about 74%. Thus, the maximum Ag_{sp} is about 73.1% of AgNP-GA, much larger than 46.6% of the AgNP-OA. It's worth noting that the space proportion of silver in the thin films will greatly affect the particle sintering and characteristics of the final products.

To continuously increase the assemble scale, the stacking method of particles should be declared. Similar to other solid thin film stacking, the nanoparticle stacking method is also combined with stacking and smoothing processes at the same time. However, the electrostatic adherence ability makes the stacking a little different from others. Fig. S7a–c (ESI†) are the schematic diagrams of the particle stacking procedure, containing adherence and smoothing steps. The stacking procedure could be described as follows: (1) the particles are in close contact on the first layer because of their electrostatic incorporation at the beginning stage. Just a little part of particles of small size can locate on the shoulder of others, otherwise, it will push away the underlying particles; (2) after keeping stacking and smoothing of AgNPs, most of the particles lie on the substrate, increasing the density of AgNPs in the first layer, making it stable to sustain the upper layer's formation. The detailed stacking procedure of AgNP-GA is shown in Fig. S7d–f (ESI†), and the TEM images with different spray cycles demonstrate consistent results as the above statements. Thus, the schematic diagrams of stacked AgNP-GA and AgNP-OA are demonstrated in Fig. 2j and k, in which the former is a little bit tighter than the latter because of the electrostatic adherence process.

To be used as conductive thin films in optoelectronic devices, AgNPs should be sintered by a soft treatment, such as low-temperature annealing. Thus, both types of AgNPs are annealed at 100 °C, and the schematic diagrams are exhibited in Fig. 2i and l. Also, the corresponding SEM images of AgNPs before and after annealing are attached below. The annealed AgNP-GA film demonstrates a continuous surface with some larger-scaled crystal-like morphology, while the OA-covered particles fail to sinter because of the thermal stable ligand and large interspace. The AFM images of as-cast and sintered

AgNP-GA films are shown in Fig. S8 (ESI†). Their root mean squares (RMS) are 5.252 nm and 12.332 nm, respectively, indicating that the roughness of the AgNP films increases after thermal sintering. The suitable roughness of Ag films can benefit diffuse reflectance, which will be investigated later. In addition, the time-varying TEM is conducted for both types of AgNPs, shown in Fig. S9 (ESI†). It can be found that the AgNP-GA easily sinters together under the e-beam illustration within 80 s, while AgNP-OA shows negligible change and remains isolated. This result can further prove that ligands can significantly influence the sintering process of AgNPs. Finally, at the end of the scale bar, the macroscopic products show a dramatic difference in their electrical and optical properties, shown in Fig. 2m. The sintering temperature of GA-based particles is lower than 100 °C, much lower than other commonly used particles, such as AgNP-OA at about 250 °C yet still with lower conductivity. To avoid the influence of particle size and interparticle distance, polyvinylpyrrolidone (PVP) and trisodium citrate (TCA) based silver nanoparticles are chosen to study the sintering behavior. The average particle sizes of AgNP-GA, AgNP-PVP, and AgNP-TCA are all around 50 nm. The TEM images of AgNP-PVP, and AgNP-TCA are demonstrated in Fig. S10 (ESI†). PVP is known as a linear polymer with many amino groups on the chain, indicating the chain of PVP will lie on the particle surface, which is different from OA. TCA is selected as a small molecular ligand. Thus, AgNP-GA, AgNP-PVP, and AgNP-TCA have similar interparticle distance and particle size, resulting in a similar space proportion of Ag in the packed AgNP films. The thermal sintering behavior is demonstrated in Fig. S11 (ESI†). The sintering temperatures of AgNP-PVP and -TCA are over 200 °C, while AgNP-GA can sinter at a temperature lower than 100 °C. As a consequence, after controlling the particle size and interparticle distance, the GA-based AgNP shows an ultralow thermal sintering temperature, owing to the unique capacity of its ligand. XRD measurements are conducted on AgNPs before and after annealing to investigate the sintering behavior (shown in Fig. S12, ESI†). After annealing, the FWHM of Ag peaks in AgNP-GA decrease, suggesting the optimized crystallization of Ag thin film. In contrast, the peaks in AgNP-OA change negligibly, suggesting a failure of sintering at low temperatures. Moreover, the sintered AgNP-GA thin film achieves a broad range of high reflectance of over 90%, much higher than AgNP-OA's (<50%). The photograph of sintered AgNP films shows a great difference, in which the GA-based product significantly turns metallic white at a low temperature of about 100 °C, while OA's shows a negligible visible change after sintering at 250 °C. Overall, the number of functional groups and carbon chain length of ligands can sequentially influence the silver particles' microstructure, stacking method, and sintering process, and finally present different characteristics of the thin film. However, the extraordinary performance of AgNP-GA thin films is not only due to the optimized stacking method and small interspace but also to some other mechanisms during sintering. Thus, a detailed analysis of the GA-based AgNP is conducted and demonstrated in the following content.

As conductive electrodes, conductivity and reflectance are essential properties. Fig. S13 (ESI†) presents the resistance and reflectance of AgNP films. Step-wised temperatures are used for annealing the AgNP films. The resistances of each sample are recorded at different periods. Fig. S14a (ESI†) is the schematic diagram of the resistance measurement. The films are deposited on the 17 mm × 17 mm glass substrates, and the resistance is measured diagonally in a 14 mm × 14 mm square area by a multimeter. A natural photograph of the resistance measurement is shown as an example in Fig. S14b (ESI†). The resistances of the as-cast films are too large to be measured. It can rapidly decrease to lower than 10 Ω with an annealing temperature higher than 100 °C in 5 min. The resistances of these samples after 15 minutes of annealing are $9.8 \times 10^5 \Omega$ for 75 °C, 135 Ω for 90 °C, 2.2 Ω for 100 °C, 0.6 Ω for 115 °C, and 0.2 Ω for 130 °C, respectively. In comparison, the evaporated silver electrode with a thickness of 100 nm has a resistance of 1.4 Ω, similar to the AgNP film annealed at 100 °C. This indicates the great potential of the AgNP film for conductive electrodes due to its excellent conductivity. The other thing to notice is that even if the temperature is 75 °C, the AgNPs can be sintered slowly but steadily. This is beneficial for temperature-sensitive applications. The reflectance spectra of the sintered AgNP films and evaporated Ag electrodes are exhibited in Fig. S13b (ESI†). The fully sintered AgNP film presents a similar reflectance to the evaporated Ag electrode in the long

wavelength region. The highest reflectance of the SAE is 96%, which is desirable for a rear electrode in photovoltaics. The slightly low reflectance of the SAE in the short wavelength region is caused by the film's original particle shape and pinhole structure, which may slightly decrease the light reabsorption in solar cells. In contrast, the surprising thing is that the diffuse reflectance of the SAE is much higher than evaporated Ag. The average diffuse reflectance in the visible region is about 25%. High reflectance haze and the aperiodic nanoscale surface undulation may benefit light absorption in the solar cells, contributed by the light scattering and light distribution manipulation.^{45–47} This favorable effect induced by SAE may cover the slight reflectance shortage and improve the final absorption efficiency of solar cells. The corresponding device's performance will be described in later content. The electrical and optical characteristics of AgNP films with different thicknesses are exhibited in Fig. S15 (ESI†). The samples are prepared by a spin-coating process with different solution drops. The reflectance of the films increased along with the drop times, and the transmittance decreased as expected. Fig. S15c (ESI†) shows the statistic diagram of the average reflectance and the corresponding sheet resistance. When only one drop solution is used in deposition, the film presents poor conductivity because of the poor coverage of AgNPs. The diffuse reflectance of one drop sample also proves this. The diffuse reflectance spectrum of the one drop sample shows a

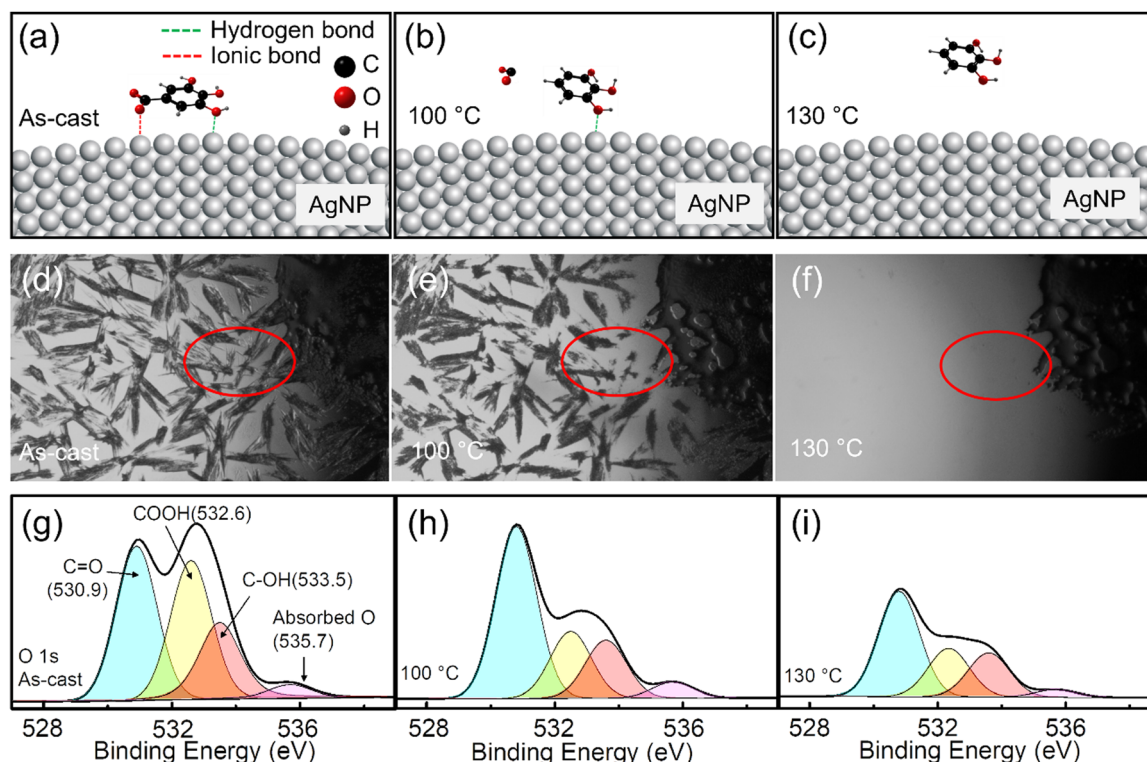


Fig. 3 (a–c) A group of schematic diagrams of the GA ligand interacting with AgNP. The decarboxylic reaction and ligand dissociation induced by the annealing process is also demonstrated in the diagram. (d–f) The optical microscope images of gallic acid before and after annealing at 100 °C and 130 °C. The spot on the right corner is used for positioning. (g–i) O 1s core-level spectra of AgNP films before and after annealing at 100 °C and 130 °C for 15 min. The relevant peak data are marked in the spectra.

wavelength-independent performance, indicating the sizeable uncovered area, which is consistent with the conductivity characterization. Two or more drops of solution can fabricate an electrode with good conductivity and suitable reflectance. The cross-section SEM shown in Fig. S15d (ESI[†]) is measured to check the thickness of the AgNP film deposited by the drop-wised spin-coating method. Twenty drops of solution spun at 2000 rpm led to a 1440 nm-thick film. In a word, the solution-processed AgNP films exhibit superior electrical and optical properties for rear electrodes.

The sintering mechanism of the AgNPs is important for selecting the specific ligand. Before analyzing the sintering mechanism, the stabilizer effect of the GA material should be described first. The carboxylic acid groups (COO[−]) in the GA molecule easily interact with the Ag and generate ionic bonds because of their negative and positive charges, respectively. At the same time, hydroxy in GA also interacts with Ag and will be connected by hydrogen bonds (shown in Fig. 3a–c).^{48–50} The bonds strongly connect the GA and AgNPs in dispersing solution, and GA coverage can prevent the aggregation of particles. Thus, sufficient GA ligands can guarantee the storage stability of AgNPs. Unlike other stabilizing ligands, which usually consist of long chain molecules, GA will conduct a decarboxylic reaction at a relatively low temperature (<100 °C), assisted by a bit of water.^{51,52} The decomposition process can be verified by the FTIR spectra of GA powers before and after annealing assisted with moisture, demonstrated in Fig. S16 (ESI[†]). After the annealing process, the gallic acid powder generates two peaks at 2358 cm^{−1} and 1717 cm^{−1}, representing CO₂ and unsaturated ester, respectively. It can verify that decarboxylation of GA occurs during the heating process and part of the carboxyl group is esterified with a hydroxy group. At the same time, the peaks of carboxyl decrease a lot, consistent with the above statement. When the ionic bonds disappeared because of the decarboxylic reaction, the surface of AgNP became unstable. After continuous annealing or annealing at a higher temperature, the hydrogen bonds between Ag and hydroxy are not strong enough to protect the AgNP surface. Pyrogallol or the remaining GA may become isolated, and the AgNPs quickly sinter with each other. This statement of thermal decomposition can be proved by the optical microscope (OM) images and X-ray photoelectron spectra (XPS) measurements, as shown in Fig. 3d–f and g–i, respectively. GA powder was annealed at different temperatures and observed by OM. The spot at the right corner was a marked point for positioning. There was a slight deformation after annealing at 100 °C, indicating that the decarboxylic reaction of GA occurred. After annealing at 130 °C, the GA almost disappeared, indicating the full decomposition of GA. Moreover, the XPS characteristics present indisputable proof for thermal decomposition. Fresh AgNP film and AgNP films annealed at different temperatures for 15 minutes are prepared to measure XPS characteristics. In Fig. S17 (ESI[†]), the peaks of Ag 3d_{5/2} and Ag 3d_{3/2} are located at 368.2 eV and 374.2 eV, respectively. No peak shift occurs during the whole annealing process. Fig. S17b and c (ESI[†]) show the O 1s and C 1s XPS spectra of the as-cast and the annealed AgNP films. The core-level spectra and relevant peak data are exhibited

in Fig. 3g–i and Fig. S18 (ESI[†]). The energies are consistent with reported values for similar chemical bonds.^{53–55} The peaks at 530.9 eV and 533.5 eV, representing C=O and C–OH, show few changes after annealing at 100 °C for 15 min. But the peak at 532.6 eV, assigned to –COOH, decreases significantly after annealing, indicating the removal of carboxyl groups. The ratio of carboxyl to the sum of hydroxyl and carbonyl decreases from 57.5% to 29.1%, demonstrating that 49% of carboxyl has been successfully decarboxylated. After annealing at 130 °C for 15 min, all the peaks decrease at a similar ratio, consistent with the statement of ligand removal. This declaration can also be proved in the C 1s core-level spectra. In the C 1s core-level spectra, four peaks can be found and assigned to corresponding bonds. The peaks at 284.6 eV, 285.8 eV, 287.5 eV, and 288.4 eV represent C=C, C–OH, C=O, and COOH, respectively. A plasmon loss peak induced by conductive materials also exists and is located at 290.8 eV. The C–OH, C=O, and COOH peaks decrease along with the increased temperature, indicating that the decarboxylic reaction occurs during the process. In conclusion, the annealing process on AgNP films can successfully produce the decarboxylic reaction and greatly remove the GA or pyrogallol ligands from the AgNP surface. Fig. S17d (ESI[†]) exhibits the Ag, C, and O mass concentrations in the as-cast and annealed AgNP films. The statistical data of the mass concentrations are listed in Table S1 (ESI[†]). The mass concentration of Ag increases from 85.60% to 88.80% and 92.37% after the 100 °C and 130 °C annealing process. In contrast, the C and O concentrations in the AgNP films significantly reduce, especially at 130 °C. This proves that the thermal treatment greatly removes the organic compounds and makes the film approach a relatively pure metallic structure. As a result, the sintered AgNP electrodes with few organic components successfully achieve high conductivity and high broadband reflectance.

Then, the solution-processed AgNP electrode (SAE) is employed in OSCs to demonstrate its suitability for electronic devices. The device structure is glass/ITO/PEDOT:PSS/D18-Cl:N3:PC₆₁BM/PEI-Zn/SAE. Fig. 4a shows the cross-section scanning electron microscope (SEM) image of the OSC. D18-Cl and N3 are employed as the absorption materials for high-performance OSCs, and the illustrative structure diagrams of D18-Cl, N3, and PC₆₁BM are exhibited in Fig. S19 (ESI[†]). PEI-Zn is chosen to replace the commonly used electron transporting layers, such as PDINO and ZnO nanoparticles, because of its polymer compounds which can sustain solution deposition of top electrodes. The amine groups in PEI-Zn are expected to interact with AgNPs and help to form an ideal interface.^{56,57} It is obvious that the AgNPs are uniformly deposited on the top of the device, and the underlying layers remain in good condition after the spray-coating deposition. The SAE is deposited by spray-coating with a portable spray gun, as shown in Fig. S20 (ESI[†]). The detailed process can be found in the Experimental section. The OSCs with evaporated silver rear electrodes are also fabricated for comparison. The statistical characteristics of the OSCs are exhibited in Fig. S21 (ESI[†]), and the relevant data are listed in Table S2 (ESI[†]). All the devices are measured under A.M. 1.5 illumination and calibrated with a standard silicon cell. The SAE-based OSCs present an average open-circuit voltage (*V*_{oc}) of

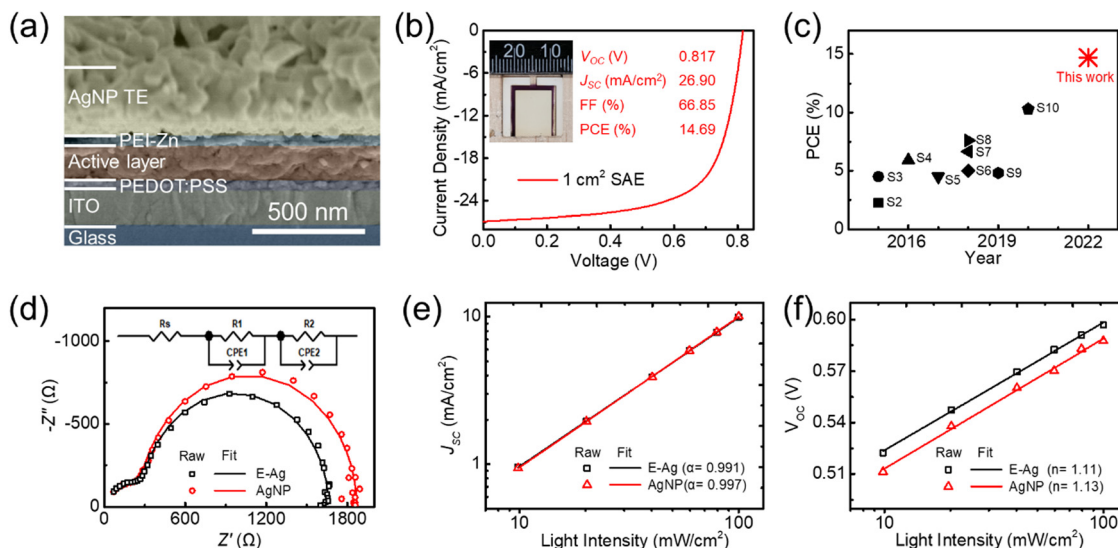


Fig. 4 (a) The cross-section SEM image of the OSC with the structure of glass/ITO/PEDOT:PSS/D18-Cl:N3:PC₆₁BM/PEI-Zn/SAE. (b) The J - V characteristics of champion large-area devices with SAE. The inset image is the top view of a large-area device with an area of 1 cm^2 . (c) The evolution of PCE for large-area OSCs ($\geq 1\text{ cm}^2$) with a solution-processed top electrode. Detailed information about the top electrodes and PCEs is summarized in Table S3 (ESI[†]). (d) Electrochemical impedance spectroscopy (EIS) of OSC devices with the structure of ITO/PEDOT:PSS/P3HT:PCBM/PEI-Zn/evaporated Ag (E-Ag) or AgNP. The inset diagram is the equivalent circuit of the OSC device. Light intensity dependence of (e) J_{SC} and (f) V_{OC} of OSCs with the structure of ITO/PEDOT:PSS/P3HT:PCBM/PEI-Zn/evaporated Ag (E-Ag) or AgNP.

0.802 V, slightly lower than the evaporated Ag-based devices. The possible reason for the decrement may be the lower work function of the rear electrodes. The work functions of SAEs are characterized by ultraviolet photoelectron spectroscopy (UPS), as presented in Fig. S22a (ESI[†]). The SAE sintered at $130\text{ }^{\circ}\text{C}$ shows a work function of -4.45 eV , slightly lower than the evaporated Ag (-4.30 eV). The schematic energy diagram of the OSC with different rear electrodes is also exhibited in Fig. S22b (ESI[†]). Rear electrodes in the conventional OSCs act as the cathode and make contact with the electron transporting layer (ETL). Generally, the small energy offset between the ETL and cathode results in a high electron extraction efficiency.^{58,59} The energy offset between PEI-Zn and SAE is larger than that between PEI-Zn and evaporated Ag, indicating slight energy loss at the interface. It is also expressed in the average fill factor, decreasing from 72% to 67.66%. However, benefiting from the excellent reflecting properties of SAEs, containing high total and diffuse reflectance, the OSCs' average current density (J_{SC}) increases from 26.59 mA cm^{-2} (evaporated Ag) to 27.04 mA cm^{-2} (SAE). The EQE spectrum and the corresponding integrated J_{SC} of the SAE-based OSCs are exhibited in Fig. S23 (ESI[†]). The integrated J_{SC} is 26.17 mA cm^{-2} , considered within the test error range. As a result, the average power conversion efficiencies (PCEs) are 15.92% for evaporated Ag and 14.67% for SAE. The J - V characteristics of champion devices with evaporated Ag and SAE are diagrammed in Fig. S21b (ESI[†]). The SAE-based OSC shows a V_{OC} of 0.815 V, J_{SC} of 27.16 mA cm^{-2} , and FF of 68.85%, contributing to the champion PCE of 15.23%. The decrement in the device performance may be mainly caused by the unsuitable work function and the imperfect interfacial contact induced by particle movement during the sintering process. The performance of the evaporation-

free device could be improved with further interfacial research. Even so, it is the highest performance of OSCs with a solution-processed top electrode to the best of our knowledge. A large area device (1 cm^2) is fabricated, and the J - V curve is shown in Fig. 4b. It presents a V_{OC} of 0.817 V, J_{SC} of 26.90 mA cm^{-2} , and FF of 66.85%, resulting in the highest PCE of 14.69%. The inset photo is the large-area OSC with SAE. Fig. 4c exhibits the evolution of large-area OSCs with various solution-processed top electrodes, such as PEDOT:PSS, AgNW, Ag ink, AgNP, and composite materials. Notably, our devices with large areas outperform all these reported ones. Therefore, the superior performance of SAE-based OSCs indicates the potential of SAE for evaporation-free OSCs and large-scale applications.

To verify the universality of this new electrode, various OSC devices are fabricated and demonstrated in Fig. S24 and Table S4 (ESI[†]). AgNP electrodes are used on the conventional and inverted structure with the device structure of ITO/PEDOT:PSS/P3HT:PCBM/ZnONP/AgNP and ITO/ZnO/P3HT:PCBM/MoO/AgNP, respectively. Different ETLs and HTLs have been used to make contact with AgNP electrodes. For example, ZnO nanoparticles and PEI-Zn work as the ETL in conventional OSCs, and MoO and PEDOT:PSS work as the HTL in inverted OSCs. In addition, three kinds of active layers are employed to present the universal nature of AgNP electrodes. All the above devices are displayed together with reference devices with evaporated Ag electrodes and show ideal power conversion efficiencies on the same level. Electrochemical impedance spectroscopy (EIS) measurement is used for analyzing the charge behavior in OSC devices, and the results are displayed in Fig. 4d. After fitting with the classical PV model, the series resistance (R_s), transfer resistance (R_1), and charge recombination resistance (R_2) can be achieved. (For the device with evaporated Ag, $R_s = 27.5\text{ }\Omega$, $R_1 = 260\text{ }\Omega$, $R_2 = 1375\text{ }\Omega$; for the device with AgNP,

$R_s = 27.8 \Omega$, $R_1 = 250 \Omega$, $R_2 = 1592 \Omega$.) The transfer resistance of the OSC device with the AgNP electrode changes little, compared to the reference device with the evaporated Ag electrode. Furthermore, the recombination resistance shows a slight and acceptable reduction. To further investigate the charge recombination dynamics, the light intensity (I_L) dependence of J - V characteristics is analyzed within the range from 10 to 100 mW cm^{-2} (shown in Fig. 4e). Then dependence of J_{SC} on the light intensity is exhibited to quantify the bimolecular recombination. The slopes of the logarithm of J_{SC} to the logarithm of I_L of the OSC with evaporated Ag and AgNP electrodes are 0.991 and 0.997, respectively, which are both close to 1. This demonstrates the absence of bimolecular recombination in both devices. Moreover, to evaluate the trap-related recombination, the dependence of V_{OC} on I_L is measured and shown in Fig. 4f. Typically, the V_{OC} and logarithm of I_L follows the relationship $V_{OC} \propto n(kT/q)\ln(I_L)$, where k is the Boltzmann's constant, T is the temperature in Kelvin, and q is the elementary charge, respectively. The fitted n for evaporated Ag and AgNP-related devices are 1.11 and 1.13, respectively. A slightly higher n value for the AgNP one represents slightly more trap-assisted recombination in this device. Overall, the AgNP-GA electrode demonstrates similar characteristics in OSCs. In addition, the operation stability of OSCs with evaporated Ag and AgNP-GA has been measured and shown in Fig. S25 (ESI†). The measurement is conducted under air conditions ($T = 30^\circ\text{C}$; RH = 60%) and under continuous light tracking at the maximum power point. The device structures are glass/ITO/PEDOT:PSS/P3HT:PCBM/PEI-Zn/evaporated Ag or AgNP. Compared with evaporated Ag, solution-processed AgNP electrodes display a little bit of poor stability at the first 80h, indicating that the AgNP electrode is not as compact as evaporated Ag and makes oxygen and moisture permeate into the device quickly. However, the long-term stability (180 h) of the two devices is similar, suggesting the AgNP electrode doesn't contribute to other chemical or interface degradations. In general, the isolation of oxygen and moisture for OSCs could be solved by ideal encapsulation. As a result, the AgNP STE will not destroy the device stability, compared with the evaporated one. These results are expected to exhibit AgNP electrode's universal for the OSC community. Furthermore, LEDs are known as important components in the optoelectronic area. An OLED device with a common structure of ITO/PEDOT:PSS/TAPC/Alq/LiF/evaporated Ag or AgNP is also exhibited in Fig. S26 (ESI†). The AgNP electrode works well on the top of the OLED device and contributes to the almost same EL spectrum as the reference device, peaking at 529 nm. The turn-on voltages are 5.3 V for evaporated Ag and 5.8 V for AgNP. A slightly higher voltage in the J - V curves indicates a slightly worse charge injection at the interface. The EQE of these two devices are 1.49% and 1.41%, respectively, which are on the same level. In conclusion, solution-processed AgNP electrodes also can perform well on top of OLED devices.

Conclusion

We have developed a strategy for electrodes for electronic applications based on a spray-coated, highly reflective AgNP

electrode with a sheet resistance of $1.6 \Omega \text{ sq}^{-1}$ and average reflectance of 92%. Fundamentally, the bottom-up process of metallic nanoparticles with different ligands is systematically studied. Ligands with compact structures and multiple functional groups, such as gallic acid, can lead to a high space proportion of metal in stacked films and compact packing during the stacking procedure. A low-temperature annealing process can rapidly sinter the AgNPs into a highly conductive electrode with high reflectance which can be robustly formed on OSCs as top electrodes without penetrating the underlying layers, assisted by the composite PEI-Zn layer. Finally, we achieve evaporation-free OSCs with a PCE of 15.23%, about 91% of the evaporated ones. In catering to the scale-up applications, a large area device (1 cm^2) presents a PCE of 14.69%, which is the highest performance of same-size evaporation-free OSCs to the best of our knowledge. Moreover, various structures of OSCs and even OLEDs have been successfully employed to verify the universality of this AgNP electrode. Overall, the integrated statement of the ligand-dominated stacking and sintering process from the bottom up is a meaningful advancement in the field of metallic nanoparticle synthesis and application. It not only contributes to realizing the high-quality solution-processed electrodes but also will benefit further research in other nanomaterial-related electronic or biological contexts.

Experimental section

Chemical materials

Silver acetate dihydrate ($\text{AgAC} \cdot 2\text{H}_2\text{O}$, 99%), gallic acid (GA, 98%), *n*-butylamine (NBA, 99%), methanol (MeOH, 99.5%), ethanol (EtOH, 99.5%), polyethylenimine (PEI, branched, M_n 25 000), zinc acetate dihydrate ($\text{ZnAC}_2 \cdot 2\text{H}_2\text{O}$, 99.9%), and 2-methoxyethanol (99%) are purchased from J&K. PEDOT:PSS (Al4083) is purchased from H.C. Starck GmbH, Germany. D18-Cl and N3 are purchased from eFlexPV Limited. Chloroform (CF, 99.9%) and 1-chloronaphthalene (CN, 97%) were purchased from Sigma-Aldrich. AgNP-PVP and AgNP-TCA are purchased from Zhongkekeyou.

AgNPs and their film formation

AgNP-GA is synthesized in a room temperature process, reduced from silver acetate dihydrate ($\text{AgAC} \cdot \text{H}_2\text{O}$). Firstly, $\text{AgAC} \cdot \text{H}_2\text{O}$ (0.167 g) was added into methanol (6 mL) and stirred for 5 min. At the same time, gallic acid (0.092 g for GA*1 or 0.276 g for GA*3) was dissolved in methanol (10 mL). The fully dissolved GA solution was quickly added into the AgAC solution dropwise and stirring was continued fiercely. After 10 minutes, *n*-butylamine (10 μL) was dropped into the stirred solution, and the solution reacted for another 10 minutes. The product was centrifuged and washed with methanol (15 mL) three times. The final sediment was dispersed in 1 mL ethanol and kept in the refrigerator before being used. The synthesis process evolves from the reported literature.⁶⁰ AgNP-OA is synthesized following a reported work in our group.²⁶

The solution-processed AgNP electrodes (SAE) are deposited by spin- or spray-coating processes. AgNP-GA solution (30 μL) is

spin-coated at 2000 rpm on the cleaned glass substrates for morphology characteristics and electrical and optical measurements if there is no special instruction. The films are annealed at different temperatures to achieve good conductivity and high reflectance.

Organic solar cell fabrication

The high-performance device structure of organic solar cells is glass/ITO/PEDOT:PSS/D18-Cl:N3/PEI-Zn/evaporated Ag or SAE. The glass/ITO substrates ($15 \Omega \text{ sq}^{-1}$) are cleaned with detergent, acetone, and ethanol by ultrasonic cleaning successively. Each cleaning process lasts for 15 minutes. The cleaned substrates are stored in ethanol for reserve. The ITO substrates are blown with N_2 and treated with ultraviolet ozone (UVO) for 15 minutes. PEDOT:PSS is deposited on the treated substrates by spin-coating at 4000 rpm for 40 s and annealed at 150°C for 20 min. After cooling down, the substrates are transferred into the N_2 -filled glovebox for the following depositions. D18-Cl:N3:PC₆₁BM (5 mg:7 mg:0.5 mg in 1 mL chloroform with 0.5 vol% 1-chloronaphthalene as the additive) solutions are prepared in advance. It is dynamically spin-coated on the PEDOT:PSS films at 2500 rpm for 30 s and annealed at 90°C for 10 min. The PEI-Zn was prepared following the reported literature (1 mg PEI, 10 μL H_2O , and 0.075 g $\text{ZnAC}_2 \cdot 2\text{H}_2\text{O}$ are dissolved in 1 mL 2-methoxyethanol).⁵⁶ The PEI-Zn precursor is deposited on the active layers by dynamic spin-coating at 3000 rpm for 30 s and annealed at 100°C for 10 min. Then, the resulting samples are deposited with top electrodes to complete the fabrication. The evaporated silver electrodes (100 nm) are deposited in a high-vacuum thermal evaporation system. SAEs are fabricated by a spin- or spray-coating process. AgNP solution (30 μL) is dynamically spin-coated at 3000 rpm drop by drop and annealed at 130°C for 5 min. A portable spray gun is used for coating the SAE. The diluted AgNP solution (300 μL , 1 : 10 in ethanol) is sprayed on the samples covered with a patterned mask. The annealing process is also conducted to sinter the electrodes.

The universal applications of SAE are prepared on various structures assisted with many materials. The preparation and deposition of each material are as follows: P3HT:PC₆₁BM (20 mg:20 mg in 1 mL dichlorobenzene) was coated at 700 rpm for 40 s and slowly grew for 1 h. PBDB-T:ITIC (10 mg:10 mg in 1 mL chlorobenzene with 0.3 vol% DIO) was coated at 2500 rpm for 40 s and annealed at 100°C for 10 min. MoO solution was prepared following previous work in our group and coated at 2500 rpm for 40 s. PEDOT:PSS (0.5% Triton) is a mixture of PEDOT:PSS and 0.5 vol% Triton X100. It was coated on the active layer at 2000 rpm for 40 s and annealed at 140°C for 10 min. ZnO s-g was prepared by dissolving zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 110 mg) in ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, 30 μL), and 2-methoxyethanol (1 mL) with vigorous stirring for 12 h. It was deposited by spin coating at 4000 rpm for 40 s and annealing at 150°C for 20 min.

Particle, thin film electrode, and device characterization

The surface charge of nanoparticles is characterized by Zeta-View Nanoparticle Tracking Analyzer. The surface morphology

of the AgNP films before and after annealing is characterized by scanning electron microscopy (SEM, Hitachi S4800 FEG), transmission electron microscopy (TEM, Philips Tecnai G2 20 S-TWIN), and atomic force microscopy (AFM, NT-MDT NTEGRA, tapping mode). The optical characteristics are measured by UV-Vis spectroscopy (SHIMADZU UV-2600). The total and diffused reflectance are measured with an integrating sphere attachment. The resistance and sheet resistance are measured by the multimeter and the four-point probe, respectively. The X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) of the AgNP films annealed at different temperatures are conducted by Physical Electronics PHI 5802. The device performances of OSCs are characterized by Keithley 2635 under AM 1.5G irradiation (100 mA cm^{-2}). The light intensity is calibrated by a silicon reference cell (ISO 17025-certified KG3-filtered). The device areas of the OSCs are 0.08 and 1 cm^2 , controlled by the shadow masks.

Conflicts of interest

There are no conflicts to declare.

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