



Review Recent Progress of Printing Technologies for High-Efficient Organic Solar Cells

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Abstract: Organic solar cells (OSCs), as a renewable energy technology that converts solar energy into electricity, have exhibited great application potential. With the rapid development of novel materials and device structures, the power conversion efficiency (PCE) of non-fullerene OSCs has been increasingly enhanced, and over 19% has currently been achieved in single-junction devices. Compared with rigid silicon cells, OSCs have the characteristics of low cost, high flexibility, lightweight, and their inherent solution processability, which enables the devices to be manufactured by using printing technology for commercial applications. In recent years, to maximize the device performance of OSCs, many efforts have been devoted to improving the morphologies and properties of the active layer through various novel printing technologies. Herein, in this review, the recent progress and applications of several popular printing technologies to fabricate high-efficient OSCs are summarized, including blade-coating, slot-die coating, gravure printing, screen printing, inkjet printing, etc. The strengths and weaknesses of each printing technology are also outlined in detail. Ultimately, the challenges and opportunities of printing technology to fabricate OSC devices in industrial manufacturing are also presented.

Keywords: organic solar cells; printing technology; blade-coating; slot-die coating; inkjet printing

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1. Introduction

The extreme climate issue caused by resource depletion and excessive carbon emissions has become increasingly serious. To achieve a global carbon-neutral demand, it is urgent to replace the utilization of traditional fossil fuels with sustainable renewable energy. Solar energy, as the largest renewable energy on earth, is the key to satisfying the future energy demand. Currently, many researchers are focused on the development of high-efficient solar cells with low cost and high stability. Nowadays, the current photovoltaic market is dominated by traditional silicon-based solar cells owing to their ultrahigh conversion efficiency and long-term stability [1]. However, the complex manufactural processes, high cost, and insufficient flexibility of the device limit their further application in portable energy devices and wearable electronics.

The third-generation solar cells, including dye-sensitized solar cells, perovskite solar cells (PSCs), and organic solar cells (OSCs), have been developed rapidly to overcome the drawbacks of traditional solar cell technologies. The OSCs, as one of the representatives, exhibit great application potential due to their mechanical flexibility, semitransparency, and wearability [2–8]. Recently, great efforts have been made over the past few decades to synthesize novel acceptors and to substitute the fullerene systems with PCE enhancements simultaneously. Fortunately, a fused ring non-fullerene acceptor (NFA) called ITIC was first reported by Zhan's group [9]. These NFAs exhibit wide light absorption ranges and tunable bandgaps and are easily modified. Since then, lots of NFAs have been synthesized, and great achievements have been obtained in the efficiency breakthrough of OSCs. The

record of power conversion efficiency (PCEs) in NFAs-OSCs has increased rapidly and has reached over 18% [10–15].

Meanwhile, research on large-scale and flexible OSCs has also attracted much attention due to their practical applications. In 2021, Huang's group [16] adopted a self-organization method by adding 2PACz into the active layer to process flexible and large-area OSCs (device area 1.0 cm^2) and achieved the highest PCE of 15.8%. More recently, Xie et al. [17]. reported 21 cm² flexible organic modules with an AgNWs-polymer transparent film as the top electrode, delivering an impressive PCE of 12.3%. However, these devices were mainly fabricated by the spin-coating method. Commonly, the spin-coating technique has been used to deposit high-quality thin films in OSCs with small areas [18–22]. The thickness of the film can be adjusted by controlling the spin-cast speed and solution viscosity. The solution was deposited on the substrate and dried quickly to avoid the risk of donor or acceptor aggregation in the wet film. Nevertheless, when it comes to large-scale substrates, the spin-coating method is inappropriate for controlling the film thickness and uniformity accurately. In addition, only a few materials remain on the substrate, most of which are spun off, resulting in a high percentage of material waste. In order to meet the requirements of future applications and industrial manufacturing, other fabrication technologies are urgently needed. Particularly, printing technologies are desirable and highly suitable for manufacturing large-area OSCs, such as blade-coating, slot-die coating, gravure printing, screen printing, inkjet printing et al. [23–27]. Recently, Wei et al. [28]. employed the slot-die method to fabricate 1 cm^2 flexible OSCs. With the fine-tuning of active layer morphology and flexible substrate properties, an efficiency of 12.16% was achieved, which was very close to the spin-coated rigid device (PCE of 12.37%). Furthermore, the same group studied the behaviors of film-dry kinetics during the slot-die process [29]. The PCE of 13.70% was obtained for 1 cm² large-area flexible OSCs. The 30 cm² flexible cells also delivered an impressive PCE of 12.20% due to the high tolerance of the film thickness. However, at present, less attention has been paid to the printing methods relative to spin coating. The performance of the lab-scale OSCs, based on printing technologies, is still lower than that of spin-coating. These printing technologies are more suitable to be adopted for the scalability and mass production of OSCs, which need to be further improved. Therefore, in this review, we summarized the recent progress of printing technologies, including bladecoating, slot-die coating, gravure printing, screen printing, inkjet printing et al. We first discussed the organic active layer and interfacial layer materials used for printing OSCs. The process, characteristics, and application of the above printing methods to fabricate the OSCs are also emphasized, including the strengths and weaknesses of each printing technology, which are outlined. In addition, the perspective for printing large-scale and flexible OSCs is also presented. We expect that this review can provide new strategies to accelerate the fabrication of OSCs with printing technology.

2. Device Structure and Materials in Organic Solar Cells

2.1. Device Architecture

The architecture of OSCs could be categorized into several types: a single-layer Schottky structure, bilayer planar heterostructure, bulk heterostructure (BHJ), and layer-by-layer (LBL) structure. For the simple single-layer structures studied in the early OSC, it is difficult to decompose the exciton into free electrons and holes due to the lack of a built-in electric field. Subsequently, a bilayer planar heterojunction solar cell (PHJ), as revealed in Figure 1a, was developed. The exciton in a PHJ device can generate charge transfer at the donor and acceptor interface, making exciton dissociation more effective. Then, when the concept of BHJ solar cells was introduced by Heeger et al. in 1995 [30], OSCs developed rapidly. The conventional structure of BHJ OSCs is shown in Figure 1b and includes a photoactive layer, hole transporting layers (HTLs), and electronic transporting layers (ETLs) coupled with electrodes. In the active layer of BHJ, the bi-continuous interpenetrating networks are formed with the mix of donor and acceptor materials, and the increasing D-A interfacial area facilitates the charge generation and separation effectively, leading

to an improvement in PCE of OSCs [31]. For now, the BHJ devices have been a major research focus in the OSC field. The solution processability of active layer materials makes it possible to form electronic organic ink, which can be adopted for efficient printing technologies [32–37].

More recently, a sequential layer-by-layer (LBL) (Figure 1c) processed solar cells emerged and provided high device efficiency [38]. Such a strategy can form a pseudo bimolecular layer (p-i-n) structure in the active layer, in which appropriate vertical phase separation can be formed to promote exciton dissociation and optimize charge transport at the corresponding electrode to reduce energy losses. The first successful examples of highly efficient OSCs based on an LBL structure were reported simultaneously by two groups in 2018. Friend et al. [39] fabricated conventional LBL OSCs based on ITO/PEDOT: PSS/NCBDT/PBDB-T/PDINO/Al. They optimize photovoltaic performance by controlling the thickness of each active layer only, and the device achieved a high PCE of 10.19%, equivalent to the 10.04% PCE obtained by BHJ OSCs. Hou et al. [40] selected PBDB-TFS1 as the polymer donor and IT-4F as the non-fullerene acceptor, where the THF solvent was used for processing IT-4F on top of the layer. It was found that when the THF solvent was treated on PBDB-TFS1 films, the quality of the film could be maintained effectively. In order to control the inter-diffusion between PBDB-TFS1 and IT-4F, O-dichlorobenzene was introduced into THF as a cosolvent. During the film preparation, o-DCB can induce IT-4F molecules to penetrate into the bottom layer successfully; therefore, the vertical phase distribution can be adjusted by changing the amount of o-DCB. As a result, researchers found that as the amount of o-DCB increases, the device efficiency of LBL OSCs gradually increases from 8.11% to 13.0%. This result demonstrated that the optimized efficiency of the LBL device is higher than that of traditional BHJ OSCs (PCE: 11.8%), which has led to the rapid development of OSCs based on an LBL structure since then.



Figure 1. Schematic architecture of (a) Bilayer planar heterojunction, (b) Bulk heterojunction, and (c) Layer-by-layer. Adapted with permission from Ref. [41]. Copyright 2021 American Chemical Society.

2.2. Active Layer Materials

The active layer materials have a direct impact on the photovoltaic performance of OSCs. Generally speaking, the active layer of heterojunction devices consists of two parts, namely the donor and acceptor material. Among them, the energy level differences between the donor and acceptor provide a certain driving force for exciton separation, which requires the cascaded bandgap of the donor and the acceptor (the LUMO energy level of the donor material is at least 0.3~0.5 eV higher than that of the acceptor). Thus, the excitons can be separated at the donor/acceptor interface effectively. In addition, to satisfy the requirements of industrial fabrication, it is important to develop materials that can be prepared with an environmentally friendly solvent without toxicity. In addition, designing the active layer materials with a thickness insensitive is also valuable for large-area device fabrication [42–45]. Table 1 summarizes the recent progress in fabricating NFA-based OSCs with various printing technologies. According to the active layer materials and fabrication techniques, we can observe that blade coating and slot-die coating are the main printing

methods to fabricate the high-efficient NFA OSCs with a maximum PCE beyond 17%, although the device areas are generally less than 1 cm², which should be further improved.

Table 1. The performance of NFA-based OSCs by printing technologie	es
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Device Structure	Active Layer Materials	Processing Method	Device Area [cm ²]	PCE [%]	Year	Ref.
ITO/ZnO/BHJ/MoO ₃ /Al	PBDB-TF:IT-4F	Blade coating	1.04	9.22	2018	[46]
ITO/ZnO/BHJ/MoO ₃ /Al	PBDB-TF:IT-4F	Blade coating	0.12	12.88	2018	[46]
ITO/PEDOT:PSS/BHJ/PFN-Br/Al	PBDB-T-SF:IT-4F	Slot-die coating	0.1	12.9	2019	[47]
ITO/PEDOT:PSS/BHJ/PFN-Br/Al	PBDB-T-SF:IT-4F	Slot-die coating	0.2	12.32	2019	[47]
ITO/PEDOT:PSS/BHJ/ZrAcac/Al	PM6:IT-4F	Blade coating	0.04	13.64	2019	[48]
ITO/PEDOT:PSS/BHJ/ZrAcac/Al	PM6:IT-4F	Blade coating	0.56	11.39	2019	[48]
ITO/ZnO/BHJ/MoO ₃ /Al	PBDB-T:i-IEICO-4F	Blade coating	0.04	11.6	2019	[49]
ITO/ZnO/BHJ/MoO _{3/} Al	PBDB-T:i-IEICO-4F	Slot-die coating	0.04	12.5	2019	[49]
ITO/PEDOT:PSS/LBL/PDINO/Al	J71:ITC6-IC	Blade coating	0.04	11.47	2019	[50]
ITO/PEDOT:PSS/LBL/PNDIT-F3N-Br/Al	PM6:Y6	Blade coating	0.04	16.35	2020	[51]
ITO/PEDOT:PSS/LBL/PNDIT-F3N-Br/Al	PM6:Y6	Blade coating	1	15.23	2020	[51]
ITO/ZnO/BHJ/MoO ₃ /Al	PM7:IT4F	Slot-die coating	0.04	13.2	2020	[52]
ITO/PEDOT:PSS/BHJ/PDINO/Al	PBDB-TF:BTP-4Cl-12	Blade coating	0.81	15.5	2020	[20]
ITO/ZnO NPs/BHJ/MoO3/Ag	PTB7-Th:EH-IDTBR	Slot-die coating	1	9.43	2020	[53]
ITO/ZnO/BHJ/MoO ₃ /Ag	PM6:Y6	Slot-die coating	5.6	15.6	2020	[54]
ITO/PEDOT:PSS/BHJ/AZO/Ag	PTB7-Th:IEICO-4F	Inkjet printing	0.1	9.5	2020	[55]
ITO/ZnO/BHJ/MoO _X /Al	PM6:Y6	Slot-die coating	0.04	15.93	2021	[56]
ITO/ZnO/BHJ/MoO _X /Al	PM6:Y6	Slot-die coating	0.56	13.91	2021	[56]
ITO/PEDOT:PSS/BHJ/PFN-Br/Ag	PBDB-T:PYT	Blade coating	0.04	15.01	2021	[57]
ITO/PEDOT:PSS/BHJ/PFN-Br/Ag	PM6:BTP-eC9	Blade coating	0.04	16.77	2021	[58]
ITO/PEDOT:PSS/BHJ/PDINO/Al	PM6:BTP-eC9	Blade coating	0.04	16.58	2022	[59]
ITO/ZnO/BHJ/MoO ₃ /Al	D18:Y6	Slot-die coating	0.04	17.13	2022	[60]
ITO/ZnO/LBL/MoO ₃ /Al	PM6:BTP-BO-4Cl	Inkjet printing	0.04	13.09	2022	[61]
ITO/ZnO/BHJ/MoO ₃ /Al	D18:BTR-Cl:Y6	Slot-die coating	0.04	17.2	2022	[62]
ITO/ZnO/BHJ/MoO ₃ /Al	D18:BTR-Cl:Y6	Slot-die coating	1	16.3	2022	[62]
ITO/AZO/LBL/MoO ₃ /Al	PM6:Y6	Blade coating	0.1	16.26	2022	[63]

For donor materials, conjugated polymers are widely used due to their wide light absorption wavelength and excellent molecular packing structure [64–66]. The design of the printable donor materials should meet the following requirements. Firstly, the materials should have strong and wide absorption in the visible and near-infrared regions, which is crucial to the improvement of the device current. Secondly, the donor material should possess higher and more balanced carrier mobility to ensure that sufficient photogenerated excitons and charges are transported to the electrodes with less recombination. Thirdly, the material should exhibit good solubility and miscibility, which is conducive to the film morphology and avoid excess aggregation in the solvent. At present, plenty of donor materials show good photovoltaic performance. Among these, the materials based on benzodithiophene are the most excellent donors, such as PM6, PM7, D18, and their derivatives, as shown in Figure 2.

The development of the acceptors has meant that a transition has been experienced from fullerene to non-fullerene materials. Figure 3 lists several frequently used NFAs. For the requirement of acceptor materials, the matchable energy levels between donor and acceptor materials are necessary. Additionally, the crystallinity and solubility of the acceptor materials should also be emphasized, which are beneficial to the formation of the appropriate domain size and phase separation in the active layer. In 2019, Zou et al. reported a new non-fullerene acceptor, Y6 [67]. This molecule replaces the sp3 hybrid carbon atom in the acceptor with the nitrogen atom in the pyrrole ring, thus, reducing energy loss and improving electron mobility effectively. Y6 and its derivatives are currently the best non-fullerene acceptors for photovoltaic performance, which greatly promotes the development of OSCs, making the energy conversion efficiency reach 15~19%. Currently,

the modification of the Y series is a hotspot in the research of OSCs. Yan et al. [68] further studied the effect of the position of alkyl chain branches on the photovoltaic performance of the device. It was found that the change in the position of alkyl chain branches could make a significant difference between the molecular stack and the morphology of the blend film. Sidechain engineering has made great achievements in controlling molecular crystallization properties, which results in the formation of high-quality films in the printing process.



Figure 2. High-efficient printable donor materials listed in Table 1.



Figure 3. High efficiency printable acceptor materials listed in Table 1.

2.3. Interfacial Layer Materials

The charge transporting layers are usually called the buffer layers or the modification layers and are sandwiched between the electrode and active layer, playing a critical role in facilitating charge extraction, trap passivation, and carrier transport. Introducing organic or inorganic interface materials to realize the ohmic contact and optimize charge transport between the active layer and electrode is an effective way to improve the performance of OSCs.

As for the conventional structure of OSCs, a PEDOT:PSS aqueous solution is the most widely used hole transporting layer material because of its excellent electrical conductivity with a high adjustability and surface wettability solution deposition [69–72]; the molecular structures of this are presented in Figure 4a. Many strategies have been devoted to modifying the properties of such conductive solutions. Recently, Howells et al. [73] introduced a polymeric fluorinated additive into PEDOT:PSS, which avoided water diffusion into the hygroscopic HTLs and protected the Al electrode from deteriorating. In addition, the fluorinated additive also allowed the HTLs to achieve suitable built-in electric field distributions to obtain a faster charge extraction. Xu's groups [74] added a multifunctional organic material (2,3-dihydroxypyridine, DOH) into the PEDOT:PSS aqueous solution as an additive, which enhanced the conductivity and hole mobility of HTLs. They found that DOH doping can facilitate the phase separation between the PEDOT and PSS chains by inducing the conformational transformation of the PEDOT chain (Figure 4b). As a result, the device efficiency based on DOH incorporation was enhanced by 20%, with a significant improvement in thermal and air stability. Kee et al. [75] added different ionic liquids into HTLs to regulate the molecular ordering of PEDOT:PSS. By controlling the counter-ion exchange between the ionic liquids and PEDOT:PSS, the molecular packing of PEDOT was rearranged (Figure 4e,f). Due to the planar and rigid molecular structures, PSS and PEDOT molecules were reassembled through a strong π - π interaction, leading to a highly ordered nanofilm of PEDOT, making the charge transfer more effective. Hou's group [76] incorporated WO_x nanoparticles into HTLs, improving the interfacial properties and device performance successfully. After blending WO_x with PEDOT:PSS, the film showed better transparency, leading to a higher short current of the OSCs. According to morphological analysis, the physical crosslinking was formed due to the fine interaction between WO_x and PEDOT:PSS. Therefore, the surface free energy and phase deviation of the thin film increased significantly when compared to the pure WO_x and pristine PEDOT:PSS as the HTL. As a result, a raising fill factor of 80.79% and PCE of 14.57% were achieved based on the PBDB-TF:IT-4F BHJ device. In addition, some other inorganic HTLs materials, including NiO_x, MoO_x, VO_x, and Ag NWs, have also been introduced into the PEDOT:PSS solution as additives to tune the work function and enhance the device performance effectively [77–80].

The modified layer between the active layer and the cathode is called the electron transporting layer. Zinc oxide (ZnO) is a wide bandgap metal oxide with high electron mobility used as the ETLs material. Hou et al. developed a high-quality printable ZnO layer through sol-gel technology. They found that the OSCs with a ZnO precursor synthesized by an n-propylamine (PA) Lewis base exhibited the best performance; it could suppress the bumps and coffee rings during the blade coating process. Thus, the 1 cm² flexible OSC fabricated with PA-ZnO ETLs showed excellent photostability and obtained a high PCE of 16.71%. Although many efforts have demonstrated that devices with ZnO ETLs show excellent photovoltaic performance [46,81-83], the amine residues from the ZnO preparation process affect the active layer materials, deteriorating the device's efficiency [84,85]. Moreover, the fluidic characteristics of ZnO ETLs in the printing process are still unclear and need further research in the application of large-area OSCs [86]. As ZnO alternatives, some alcohol-soluble organic ETL materials with high conductivity could afford a suitable energy level alignment at the electrode interface. The naphthalene diimide (NDI), perylene diimide (PDI), and their derivatives are also most representative of ETLs. Zhang et al. [87] reported an aliphatic amino-functionalized PDI derivative named PDINN. It not only has excellent electronic transmission performance but also has high crystallinity. When introducing PDINN as the ETLs, the charge transfer performance of the device is effectively improved, and the OSC based on PM6:Y6 achieved a high PCE of 17.23%. Liu et al. [88] introduced imidazole functional groups into the molecules to substitute the amine terminal group. Two novel interlayers, molecular NDI-M and PDI-Ms, were synthesized successfully by a condensation reaction. Compared to the molecular with amine groups, the imidazole-group-based molecules of NDI-M and PDI-M have deeper energy levels, as shown in Figure 4c, which facilitated the electron extraction and enhanced the charge transport at the interface. The devices based on D18-Cl:Y6:PC₇₁BM with the PDI-M as ETLs obtained a high PCE of 17.98%. Figure 4d–f shows the versatility and applicability of these imidazole-functionalized small molecules in different OSCs.



Figure 4. (a) Molecular structures of PEDOT and PSS. (b) The conformational transformation of PEDOT and PSS chains. (c) UPS of various ETLs (d-f), J-V curves of different OSCs with and w/o PDI-M as ETL. Adapted with permission from Ref. [88]. Copyright 2021 American Chemical Society.

3. Methods for Printing Technologies

Recently, a variety of film-forming technologies for solution-processed OSCs have been developed. The high-efficiency OSCs are basically manufactured by the spin-coating method. Despite the excellent behaviors of lab-scaling devices with spin-casts, recently, this method has not been favorable for upscale production [89]. When it comes to large substrates, the limitation of the spin process leads to inhomogeneous thickness at the edge of the blend films, affecting the device's performance. In addition, a large amount of solution wasted in the spin coating process further increases the costs. Therefore, for the mass and scalability production of OSCs, upscale printing fabrication technologies are urgently needed as shown in Figure 5. One type of printing method is when the mixed solution is transferred to the substrate by pouring, spraying, or casting. There is no contact between the coating head and the substrate. These methods can be divided into blade coating, slot-die coating, spray coating et al. On the other hand, the gravure printing, screen printing, flexographic printing, et al. methods are stamping processes in which the solution and substrate contact directly and can form two-dimensional patterns. In addition, inkjet printing has favorable applications for producing complex patterns. At present, fabrication technologies allow mechanical flexibility and solution-processable materials to be printed on flexible or rigid substrates, which are simple, efficient, and environmentally friendly methods for film fabrication and can also be integrated with Roll-to-Roll processing [90–92].



Figure 5. Schematic representations of: (a) Blade coating and (b) Slot-die coating. Adapted with permission from Ref. [23]. Copyright 2022 Wiley–VCH (c) Inkjet printing, (d) Screen printing, and (e) Gravure printing. Adapted with permission from Ref. [16]. Copyright 2022 Chinese Chemical Society.

3.1. Blade Coating

Blade-coating, known as doctor-blade, is a promising printing technique for preparing large-scale films. It is also a continuous fabrication process and is wildly used in laboratory preparation with the advantages of equipment simplicity, sufficient material utilization, and tunable parameters [93]. During the coating process, the precursor solution is deposited in front of the blade on the heating plate then the blade moves parallel to the substrate at a certain rate to disperse the solution and form a wet film. In order to obtain high-quality active layers, the properties of the film can be controlled by adjusting the parameter of the coating speed, solution concentration, solution species, plate temperature et al. The thickness (d) of the dry film can be calculated from the following empirical formula:

$$l = \frac{1}{2} \left(g \frac{c}{\rho} \right) \tag{1}$$

where "g" is the distance between the blade and substrate, "c" is the concentration of the solution, and " ρ " is the density of the final dry film. It is noteworthy that after coating, the wet film requires a long time to solidify. During the phase transition process, the solution tends to aggregate or self-assemble, especially for polymer materials, which leads to poor film morphology [51,63,94,95]. Therefore, great efforts have been devoted to the study of a mechanism of film formation in the blade coating process. This printing technique was first applied to the fullerene system by Mens et al. [96] to study the crystallization and phase separation of the blend film based on MDMO-PPV and PCBM. According to the results of solid-state NMR spectroscopy, they found that PCBM exhibited higher crystallinity in the blade coating method than in spin coating, which was related to the slower solvent evaporation rate in the blade coating process. In 2018, Ma et al. [46] developed the blade coating method for preparing inverted non-fullerene solar cells. The device structure with ITO/ZnO/PBDB-TF:IT-4F/MoO₃/Al delivered a PCE of 12.88% by improving the surface morphology of the ZnO buffer layer. Considering the differences in the spreading force and drying dynamics between spin-coating and blade coating, particularly in the preparation of large-area devices. Thus, they fabricated a smoother ZnO layer successfully to enhance the interfacial contact with the active layer, and consequently, led to a higher performance for the blade coating device. In the same years, Zhao et al. [97] also used the blade coating method to fabricate PBTA-TF:IT-M-based and PBDB-TF:IT-4F-based solar cells via a vacuum-assisted annealing (VAA) strategy, as depicted in Figure 6a. A similar phase separation of the OSCs was observed in both blade coating and spin-casting methods, with the maximum PCEs of 10.72% and 13.55%, respectively (Figure 6b). Due to the effect of the VAA process, the unfavorable morphology caused by the prolonged drying process was suppressed, and the large-area OSCs module with a 12.6 cm² large area based on PBDB-TF: IT-4F attained a PCE of 10.21% with a V_{oc} of 2.56 V, J_{sc} of 6.23 mA cm⁻² and FF of 64.02%, which proved that the VAA method is a feasible way for blade coating large-area modules. On the basis of these previous studies, attention has been paid to the defects in film-forming during the coating process, such as inhomogeneous phase distribution, selfaggregation, and large phase separation. Strategies have been put forward to improve fluid flow and adjust film wettability, such as selecting solvents, adding additives, or controlling temperature et al. [56,87,94,97–99]. For example, Li et al. [97] developed a green solvent O-xylene for the eco-friendly printing of OSCs via blade-coating under high-temperature conditions. The excessive aggregation of the Y6 acceptor was inhibited effectively under 90 $^{\circ}$ C during the coating process, which shortened the drying period of the wet film. They also introduced 1,2-dimethylnaphthalene as the solvent additive to facilitate the crystallinity of the blend films. Contributing to enhanced photon absorption and reduced energy loss, the device based on PM6:Y6 obtained a PCE of 15.51%. In addition, large-area solar cells with 1.00 cm² were fabricated in the air, delivering a high PCE of 13.87%. More recently, Yuan et al. [56] designed the micro cylinder arrays patterned blade in order to control the fluid flow and optimize the morphology of the PM6:Y6 blend films, as represented in Figure 6c–e. They discovered that the arrays of the patterned blade had changed the fluid flow into a stable, unidirectional, and external flow type, which enhanced the rate of the extensional and shear strain. Thus, the polymer chains of PM6 were effectively stretched and aligned, leading to favorable phase separation, as shown in Figure 6f. As a result, the blend films used a patterned blade coating method via a lower coating speed and exhibited enhanced crystallinity and optimized morphology when compared to the normal blade coating. In addition, this novel strategy improved the exciton dissociation and charge transport efficiency, which was also applied in the fabrication of large-area devices successfully.

Recently, the sequential solution deposition of the layer-by-layer structure has been demonstrated as a promising way to achieve high-performance OSCs, and blade coating is also widely applied in the fabrication of this type of device. Sun et al. [50] reported an LBL processing approach using a sequential blade coating method to investigate the differences with the BHJ structure and studied morphology, photophysical dynamics, and device performance systematically (Figure 7a). They reported that the vertical distribution of the donor and acceptor brought by LBL processing is more advantageous than that of BHJ, which not only facilitated the charge transfer but also enhanced the stability of the devices. Several non-fullerene blend systems fabricated by this technique all exhibited higher efficiency and lower voltage loss, which indicated the excellent universality of sequential blade coating and its compatibility with different active layer materials. It is worth noting that the interpenetrating network structure formed in BHJ is generated by a spontaneous nanophase separation, which is metastable. When the morphology is adjusted to the thermodynamic equilibrium state, a large-scale phase separation can be observed. As a result, the device performance, especially for large-area solar cells, deteriorates [38]. Under this consideration, Min et al. [51] fabricated LBL devices based on PM6:Y6 with a sequential blade coating method, achieving a high efficiency of 16.35% for a small area (0.04 cm²). The OSCs, as shown in Figure 7b,c, was better than the BHJ-bladed devices. They found that when introducing the LBL processing, the blend films could exhibit higher absorption and an obviously enhanced charge transport ability. In order to further explore the universality of this printing technique, other non-fullerene systems, PM6:Y62Cl, PTQ10:Y6, and PM6:Y6-C2, were also selected. Benefiting from the physical dynamics to form proper surface uniformity for the sequential blade coating films, they applied this strategy to fabricate large-scale solar modules (Figure 7d). The 11.52 cm² module delivered an impressive PCE of 11.86% with a $V_{\rm oc}$ of 3.20 V, $J_{\rm sc}$ of 6.41 mA cm⁻², and an FF of 57.85%, which is the highest efficiency of large-area OSCs. These results demonstrate that the LBL printing technique shows great potential for the high performance of OSCs with mass production and a decrease in the PCE roll-off effect. Additionally, Li et al. [63] deeply studied the mechanism of film formation by adopting a reversible and LBL deposition method with sequential twice forward/reverse blade-coating (Figure 8a). The viscosity of PM6 in chloroform is related to the shear rate of the fluid, showing the feature of non-Newtonian fluid. During the coating process, the inhomogeneous viscosity of PM6 leads to poor mass distribution on the substrates. Thus, they developed an RS-LBL strategy to compensate for PM6 mass loss during printing, resulting in more uniform film thickness and higher light absorption. Benefiting from the uniform phase distribution, the active layer exhibited excellent face-on stacking and a PCE of 13.47% with an enhanced $V_{\rm oc}$ of 9.90 V, J_{sc} of 1.93 mA cm⁻², and FF of 70.53% was achieved in the large-area (36 cm²) solar modules (seen in Figure 8b-e).



Figure 6. (a) Schematic illustration of blade-coated OSCs and vacuum-assisted annealing method. (b) PCE of various non-fullerene systems via different post-treatment methods. Adapted with permission from Ref. [97]. Copyright 2019 The Royal Society of Chemistry. (c) Schematic illustration of patterned blade coating. (d) Typical scanning electron microscopy (SEM) image of the circular patterned coating blade. (e) Cross-sectional SEM image of the circular patterned coating blade. (f) Schematic diagram of conformational changes in polymer and non-fullerene small molecules in stretching and shearing field Adapted with permission from Ref. [56]. Copyright 2021 Wiley–VCH.



Figure 7. (**a**) Schematic of device architecture with different active layers and sequential blade coating method. Adapted with permission from Ref. [50]. Copyright 2019 the Royal Society of Chemistry. (**b**) Schematic illustration of the LBL blade coating and device architecture of OSCs [87], (**c**) *J*–*V* curves of BHJ and LBL devices using blade coating method. (**d**) Large-area solar modules for blade coating process. Adapted with permission from Ref. [51]. Copyright 2019 Elsevier Inc.

3.2. Slot-Die Coating

Slot-die coating is another printing technique that forms stripe patterns by controlling ink properties with excellent reproducibility, which is very suitable for printing multi-layer OSCs. The slot-die coating head is an ink reservoir consisting of two movable metal blades, a meniscus guide, and a gasket to support the pressurization of the ink. During the coating process, ink is provided through the coating head with a pump continuously and is deposited between the tip of the head and the substrate. Then, the coating head simply moves along the substrate direction to print a wet film. Similar to the film formation mechanism in the blade coating, the film thickness can be accurately determined by controlling the ink feeding rate, or the speed of the slot die head, which can be calculated as follows:

$$d = \frac{f}{Sw}\frac{c}{\rho} \tag{2}$$

where "*f*" is the flow rate of the ink, "*S*" is the coated speed, "*w*" is the coated width, "*c*" is the concentration of the ink, and " ρ " is the density of the final dry film. In addition, the slot-die coating is a closed feeding system, and it can efficiently prevent ink pollution and excessive evaporation during coating, which is critical for future industrial preparations [100–102]. Researchers are devoted to improving film quality and developing high-performance devices by the applied slot-die coating method. Zhao et al. [54] reported a slot-die coating process to fabricate hydrocarbon-based solvent solar cells with the device inverted structure of ITO/ZnO/PM6:Y6/MoO₃/Al. The aggregation behaviors of PM6 and Y6 in each solvent solution were different and exhibited temperature dependence (Figure 9a–c). For the coated films prepared in chlorobenzene, 1,2,4-trimethylbenzene, and ortho-xylene as solvents, they all exhibited higher crystallinity and appropriate morphology, resulting in enhanced and balanced charge transport along with reduced nonradiative losses. By optimizing the process temperature of slot-die coating, they achieved an impressive PCE of 15.2%, 15.4%, and 15.6%, respectively, which proved this scalable printing technique to be suitable for large-scale and industrial and environmentally friendly OSC production. To further understand the influence of solvents during the coating process, Yang et al. [103] used a sequential slot-die coating approach to prepare PM6:Y6 blend films by adopting two different kinds of boiling point solvents: chlorobenzene and chloroform. The donor layer was coated using high-boiling chlorobenzene first, while the acceptor dissolved in chloroform was slot-die-coated on the donor layer, in which the vertical phase separation was formed. They discovered that the film formation process of different solvents accompanied by different drying kinetics affected the morphology of the active layer (Figure 9d–e). The high-boiling solvent with less evaporation remained in the donor layer when the acceptor Y6 was deposited sequentially. The well blend of the PM6:Y6 film achieved an optimized vertical phase distribution and impressive interpenetrating network structure. As a result, the sequential slot-die coated device with two different solvents delivered a PCE of up to 14.42%, which is higher than the ones in traditional single solvents. Recently, Wei et al. [29] studied the film-dry kinetic during the slot-die coating process systematically by selecting two different NFAs: Qx-1 and Qx-2. Through in situ UV-vis absorption measurements, they found that Qx-1 maintained an appropriate aggregation with suitable crystallization during the drying process, while Qx-2 exhibited excessive aggregation, resulting in poor device performance, as shown in Figure 9d,e. The benefit from the desirable domain size of QX-1 and high thickness tolerance of blend films was that the 1 cm² flexible OSC based on PM6: Qx-1 via a slot-die coating method delivered a PCE of 13.70% and FF of 71%. Furthermore, they also fabricated 30 cm² large-area OSC modules along with an outstanding PCE of 12.20% and superior storage stability of over 6000 h. Despite the high materials utilization and low waste of this printing technique, large amounts of ink are needed to fill in the slot before coating. Therefore, it is an inappropriate method for preparing high-cost ink coating [104].



Figure 8. Schematic diagram of (a) RS–LBL fabrication. (b) Large-area OSC modules. (c) The J-V curves of the OSC; (d) The photograph of the blade-coated 36 cm² OSC modules on a 10 × 10 cm² substrate. (e) The reported PCEs of binary OSC modules with an active area over 30 cm². Adapted with permission from Ref. [63]. Copyright 2022 Wiley–VCH.



Figure 9. Temperature-dependent UV–vis absorption spectra of PM6 and Y6 in (**a**) CB, (**b**) o–XY, and (**c**) TMB. Adapted with permission from Ref. [54]. Copyright 2020 Wiley–VCH. (**d**) Schematic illustration of in situ UV–vis absorption measurement and slot-die coating process, (**e**) Diagram of the morphology of PM6: Qx-1 and PM6: Qx-2. Adapted with permission from Ref. [29]. Copyright 2022 Wiley–VCH.

3.3. Inkjet Printing

Inkjet printing is a digitally controlled printing technique and is widely used to fabricate the functional layer in OSCs with the advantages of low material waste, patternable preparation, and a maskless and contact-free process. The operating principle can be divided into the formation and spraying of liquid drops, the position, and diffusion of drops on the substrate, the evaporation of the solvent, and the formation of dry film. The ink is deposited on the substrate through a nozzle. Additionally, the size of the droplet can be well controlled by heating or mechanical compression. When the substrate moves forward, the wet film is prepared by moving the printing head in the transverse direction. There are two common inkjet printing models used to generate droplets, which are continuous inkjet printing (CIJ) and drop-on-demand (DoD)' [105,106], as shown in Figure 10a,b, respectively. In CIJ, the ink is sprayed from the nozzle, and the continuous droplets are charged by the electrode. When passing through the deflection plate, the electrostatic field deflects the charged ink droplets to a certain angle and then deposits them on the substrate selectively. In the DoD mode, it usually requires several printing heads, in which the ink droplets are formed by the pressure pulse of the piezoelectric stimulation or a thermal inkjet bubble. The droplets are sprayed from the nozzle only when demanded. Although CIJ is a fast-printing method, its complex operation and low printing resolution limit its application in large-area device fabrications. DoD technology is favored for the industrial production of functional materials. The DoD inkjet printing is stable for growing droplets to avoid the secondary droplets or satellite spots that influence the film properties. The DoD inkjet is a nearly no-waste process with high material utilization. The behaviors of ink droplets are related to the fluid properties, such as the viscosity, density, or surface tension of the ink, which should be adjusted to satisfy the printing requirements, and it can be characterized as Z, which is a dimensionless inverse Oh number as described in the following equation:

$$Z = \frac{1}{Oh} = \frac{\sqrt{\rho d\gamma}}{\eta} \tag{3}$$

where " ρ " is density, " γ " is the surface tension, "*d*" is the nozzle diameter and " η " is the viscosity of the solution. Generally, the ink with a *Z* value in the range of 1 < *Z* < 10 can

form stable droplets, which is suitable for inkjet printing [107–110]. For example, Corzo et al. [111] reported that they developed the DoD inkjet printing to fabricate the P3HT:O-IDTBR BHJ device, yielding an impressive PCE of up to 6.47%, which was the first time the inkjet employed a printing technique into the NFA system for OSCs. According to rheological properties, they dissolved the P3HT:O-IDTBR blend in chlorobenzene-based and hydrocarbon-based ink, respectively, to achieve consistent jetting and optimize the droplet spacing and deposition temperature to form uniform films. In addition, they fabricated a 2.2 cm² large-area free-form solar cell by digital inkjet printing, delivering a PCE of 4.76%. Later, the same group yielded a PCE of up to 12.4% for opaque devices and 9.5% for semitransparent devices, where a PTB7-Th: IEICO-4F system was prepared via inkjet printing [55]. More recently, Chen et al. [61] developed LBL inkjet printing with sequential deposition to balance the film aggregation and optimize the vertical phase separation. Through the in-depth investigation of the mechanism in film formation during the inkjet printing possess, they found that the distributions of the donor and acceptor were ununiform on the surface. The higher solubility of ITIC-4F tended to be redissolved when the adjacent droplets coalescent during the spraying process. On the other hand, the donor showed less redissolution, as shown in Figure 10c–e. Thus, the ITIC-4F is preferred to enrich at the center of the printed lines, and the PBDB-T-2F was nearly uniform in the direction of printing, which exhibited a periodical phase separation distribution on the film. Due to the optimization of the dropping temperature and morphology, the molecular aggregation was suppressed efficiently, and exciton dissociation was also enhanced in non-fullerene OSCs based on PBDB-T-2F: BTP-BO-4Cl. As a result, the best OSC delivered an average PCE of 13.09%, which is the highest value of lab-scale OSCs fabricated by a sequential inkjet printing method, as depicted in Figure 10f-g.



Figure 10. Schematic diagrams of (**a**) Continuous inkjet printing (CIJ), (**b**) Drop-on-demand (DOD) inkjet printing. Adapted with permission from Ref. [106]. Copyright 2019 The Royal Society of Chemistry; (**c**,**d**) Photographs of the ink drop and printed lines when printed at 50 °C. (**e**) The schematic diagram of droplet coalesces during inkjet printing with DS of 40 μ m. (**f**) *J*–*V* curves of PBDB-T-2F: BTP–BO–4Cl devices from one-step and LBL–IJP. (**g**) The histogram of the one-step and LBL–IJP processed OSCs. Adapted with permission from Ref. [61]. Copyright 2022 Wiley–VCH.

3.4. Screen Printing

Screen printing is a versatile technique used to print patterns through the screen and supports full 2D printing films with high material utilization. Differing from other printing technologies, screen printing usually requires high-viscosity ink that enables the printing of nanoscale films, especially for some high-conductivity electrodes. Its reproducibility is affected by paste properties or screen tension [16,23,112–116]. Generally, screen printing can be divided into flatbed screen printing and rotary screen printing. Figure 11a depicts a schematic diagram of a flatbed screen printing method designed for printing on a flat substrate. Flatbed screen printing is a continuous process in which the ink is dispersed on the screen first, and the screen is contacted with the top of the substrate, then a squeegee is moved across the screen. Therefore, the ink is shear thin and transferred to the substrate to form a specific pattern. This printing process can be further repeated by raising the screen to move forward. Rotary screen printing, as shown in Figure 11b, is more suitable for high-throughput printing production owing to its higher printing speed and resolution than flatbed screen printing. In the process of rotary screen printing, the screen includes ink, squeegee, and patterns assembled as a cylinder, which rotates together with the substrate. The ink is pushed into the mesh through the stationary squeegee to reproduce the pattern. It allows the printing speeds to reach a high level (over 100 m min⁻¹). However, in terms of pattern operability, flatbed screen printing exhibits more advantages in printing flexibility and interval control than rotary. Krebs et al. [117], in 2009, first reported the preparation of OSCs by using a screen printing method. They discovered that the ink viscosity and solvent volatility should meet the requirements to screen print successfully. High viscosity is a prerequisite for ink through the mesh as smooth and low volatility can help the ink disperse on the substrate completely instead of drying at the screen. They developed thermos-cleavable solvents to solve the ink problem and prepared devices based on P3MHOCT. Screen printing is also used for fabricating conventional fullerene-based OSCs, especially for the donor polymer material of MEH-PPV [118]. At present, no records have been found for preparing the non-fullerene active layer by using the screen printing method. However, this technique exhibits advantages in printing electrode or transport layer materials [112,113,119]. Figure 11d describes the schematic of a fully roll-to-roll device. The transparent conductor of PEDOT:PSS was printed fully by the using flatbed screen printing method, while the silver electrode was covered on it by the same strategy, as shown in Figure 11c.

3.5. Gravure Printing

Gravure printing is a mature printing technique that produces high-resolution patterns, which is widely used in package and graphic publishing. Gravure printing is composed of two cylinders, called the gravure cylinder and the impression cylinder. During the printing process, the gravure cylinder with engraving patterns is embedded with an ink duct. The pattern of the cylinder determines the effective area for ink transfer. With the rotation of the gravure cylinder, the excess ink is scraped off by the blade. Meanwhile, the substrate completes the transfer of the ink by contacting the impression cylinder to form the pattern. The thickness of the films is determined by the depth of the mesh hole on the gravure cylinder. For gravure printing, the inks usually have relatively low viscosity to support printing with high speeds over 1000 m/min. Therefore, low boiling point solvents are widely used as ink solvents to enable the fast drying of the printed wet film [120–122]. However, gravure printing is still a challenging technique for OSCs. It tends to form a relatively thin layer. Until now, there have been few reports on the active layers deposited using this method. Similar to screen printing, the complex patterns in gravure printing will increase the cost of the fabrication. This fixed pattern mode is ideal for printing electrode materials or transport layers [123–126]. Figure 11e describes the gravure printing process of the silver-nanowire-based transparent electrodes by Wang et al. They prepared 1 cm² flexible solar cells based on PM6: Y6, as shown in Figure 11d, with an efficiency of 13.61%,



demonstrating the high potential of gravure printing in the prepattern and mass fabrication of the devices.

Figure 11. Schematic diagrams of (**a**) Flatbed screen printing, (**b**) Rotary screen printing. Adapted with permission from Ref. [112]. Copyright 2016 Wiley–VCH. (**c**) Fully roll-to-roll flexible device, (**d**) Device structure of the 1 cm² flexible OSCs. Adapted with permission from Ref. [119]. Copyright 2020 IOP Publishing Ltd. (**e**) Silver nanowire electrodes fabricated by high-speed gravure printing process. Adapted with permission from Ref. [126]. Copyright 2020 Wiley–VCH.

4. Conclusions and Prospects

With the rapid development of solvent-processed OSCs, it is necessary to replace the fabrication technique from the laboratory-scale spin coating method with efficient printing technologies, which are more compatible with the high-throughput mass production of devices in the future. In this review, we have summarized the recent progress of printing technologies, including blade coating, slot-die coating, inkjet printing, screen printing, and gravure printing, and made comparisons on their ink requirements, printing speed, and pattern dimensions as shown in Table 2. In view of all the printing technologies described in this review, blade coating and slot-die coating are the most desirable technologies for the scalable fabrication of large-area OSCs, showing high efficiency. The blade coating process is relatively simple and can print at high speed with low material waste. Similar to blade coating, slot-die coating can print one-dimensional patterns, which are favorable for sequential deposition processes. Inkjet printing has merits in changeable digital printing patterns and the contactless process. Although there are some achievements made in lab-scale OSCs, the relatively slow printing speed and complex ink preparation inhibit the further application of large-area OSCs. As for screen printing, this printing method is suitable for highly viscous ink, which contrasts gravure printing with a low viscosity of the ink. Due to the high requirement for ink, there are few reports on active layers fabricated by these two technologies. Instead, both printing methods are ideal for the fabrication of electrodes of large-area OSC modules

 Table 2. The comparison of different fabrication technologies.

Technique	Ink Preparation	Ink Viscosity	Ink Usage Rate	Speed	Pattern ¹
Spin coating	Simple	Low	Low	-	0
Blade coating	Simple	Low	High	Low-High	0
Slot-die coating	Simple	Low-High	High	High	1
Screen printing	Moderate	High	High	Medium	2
Gravure printing	Difficult	Low	High	High	2
Inkjet printing	Moderate	Low	High	Medium	2

Pattern¹: 0 (0-dimensional); 1 (1-dimensional); 2 (2-dimensional).

Although the efficiency of the printed OSCs fabricated via these technologies has been improved continuously, the mechanism of the film formation through these printing methods is still unclear, and there is a big gap in device efficiency between large and small-area devices. Thus, we propose several directions that deserve more attention. Firstly, we should recognize that most of the high-efficient materials used in OSCs require complex synthesis and treatment processes, which are unfavorable to the industrial fabrication of the devices. The design of organic materials with simple synthesis steps and easy postprocessing is always crucial for the manufacture of printable OSCs. Secondly, the film morphology and quality determine the device performance directly. How to control fluid flow during the printing process is still a problem. It is of great significance to investigate the hydrodynamics and crystallization kinetics of active layer ink for obtaining high-quality printed films. Additive and solvent engineering have also been demonstrated as effective strategies to improve the film's quality. In addition, the application of non-toxic green solvents with a high boiling point can reduce the solution aggregation during the printing process and prevent the pollution caused by halogen solvents, which are important research topics in printable OSCs. Thirdly, the low stability of organic photovoltaic materials is a big challenge which needs to be addressed before the wide application and commercialization of OSCs. In order to improve the lifetime of devices and reduce their sensitivity to light, heat, or other complex conditions, the modification of active layer materials and transport layer materials are effective approaches to improve the device's stability. Additionally, for large-area ITO-free flexible OSCs, it is quite necessary to maintain their excellent mechanical stability by developing novel packaging techniques. These bottlenecks are expected to be solved to promote the application of printing technologies toward the commercialization of OSCs.

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