


Overview of printing and coating techniques in the production of organic photovoltaic cells

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Funding information

Coordenação de Aperfeiçoamento de
Pessoal de Nível Superior, Grant/Award
Number: 001

Summary

The organic photovoltaic cell (OPV) is composed of multiple layers, and some printing and coating techniques are more suitable than others for a certain type of layer. This paper aims to characterize and compare the most relevant coating and printing techniques that can be used in the manufacture of OPVs. Extensive bibliographic research was carried out on articles published from 1998 to 2020 to identify various aspects OPV, such as the principle of operation, advantages, disadvantages, and which layers can be printed by each technique. The results show that the most used method for the processing of OPVs is spin-coating. In the studies found, rotation was used to coat the active layer, the electron transport layer, and the hole transport layer. The techniques of pad printing, casting, and meniscus are considered useful in the processing of the active layer. Regarding the deposition of the active layer, hole transport layer, electron transport layer, and anode, the rotogravure, crack matrix, spraying, and brushing techniques were satisfactory. Flexography has been used to form the active layer, electron transport layer, and anode. Screen printing, inkjet printing, and knife/blade coating were used in the processing of the active layer, hole transport layer, electron transport layer, anode, and cathode. All the double slot die coating, curtain coating, and slide coating allows simultaneous processing of multiple layers. Techniques compatible with roll-to-roll processing are more likely to be at the center of OPVs in the future, thus making solar photovoltaic technology more competitive.

KEYWORDS

coating techniques, organic photovoltaic cell, printing techniques

1 | INTRODUCTION

Technological mapping and prospecting studies show that organic photovoltaic cells are a potential technology in the generation of electric energy in line with the

planet's sustainability theme. However, for this technology to be technically and commercially viable, technological advances and incentives are required.^{1,2} In recent years, the need for fast and inexpensive processing of large areas of organic thin films has become an

increasingly important objective within a series of research fields that emerged from the idea that the processing of organic electronics solutions has the potential for that. When research on organic photovoltaic cells (OPV) focuses on a particular aspect, such as conversion efficiency, other equally important areas of research can be overlooked while they share the same importance when it comes to achieving the goal of stable cells, efficient and low cost, prepared by very fast processing techniques.^{3–5} Sampaio and González⁶ state that there is a continuous effort to improve efficiency and reduce solar cell costs.

A material that gives rise to devices with greater efficiency is therefore of little importance if the operation of this device is not stable or if the manufacturing process is difficult. That is, the practical application of organic photovoltaics depends on high productivity processing. After all, if large-scale processing proves problematic or impossible, the concept of OPVs would become a scientific curiosity, with little consequence for humanity. Thus, more research and development efforts in roll-to-roll processing are needed to meet large-area manufacturing and industrial demands, as well as must be treated and taken into account cost, operational stability, and energy conversion efficiency to be addressed and taken into account before any importance can be attributed to OPVs.^{3–5,7–10}

It should be noted that the organic photovoltaic cell is composed of several layer,⁷ and some printing and coating techniques are more suitable than others for a certain type of layer.⁸ The printing and coating techniques available cover a wide range of application methods. Previous studies^{7,9,11,12} reviewed the main techniques.

One of the challenges today is to identify the ideal coating and printing techniques for each layer. The ideal process should involve processing the solution of all layers on flexible substrates by combining the least number of coating and printing steps possible. The process must be low cost, must be free of toxic solvents and chemicals, and the cell must have a low environmental impact and a high degree of recyclability.⁷

Theoretical research on a wide range of OPV printing and coating techniques has a gap in relation to the historical period in which the last investigation was carried out in 2016. In view of the above, this paper aims to characterize and compare the most relevant printing and coating techniques that can be used in the manufacture of OPVs. For this purpose, an extensive bibliographic research was carried out on the articles published from 1998 to 2020. Therefore, the novelty of this work is the identification and compilation, in a single material, of several aspects, such as the principle of operation, advantages, disadvantages, and which layers can be printed by each technique.

In addition to this introduction, the article consists of a section on coating techniques and printing of organic photovoltaic cells, followed by conclusions and perspectives on the topic and suggestions for future studies.

2 | COATING AND PRINTING TECHNIQUES FOR ORGANIC PHOTOVOLTAIC CELLS

Organic photovoltaic cells typically comprise a multilayer structure (Figure 1) in which each layer in the stack can be formed by an individual film-forming technique.¹²

Some OPVs use vacuum processing to manufacture one or more layers that make up the cell. Although vacuum processing is not an impossible technique to be used in mass production of OPVs, some challenges need to be overcome in terms of processing speed, capital investment, technical performance of the processing equipment, and direct process energy. This fact shows that vacuum processing must be avoided and layers must be printed using methods that provide a high degree of precision and technical performance.¹³

Determining which technique is most suitable for the manufacture of organic photovoltaic cell modules in terms of technical performance, use of materials, and processing speed is not an easy task. Commercial printing and coating techniques were developed to process OPV modules for large areas.^{8,13,14} In Sections 2.1 and 2.2 are described, respectively, some printing and coating techniques for the processing of organic photovoltaic cells.

2.1 | Printing techniques

In printing, through the reversal action, a layer of ink is transferred from a stamp to a substrate, that is, in general, there is physical contact between the stamp and the

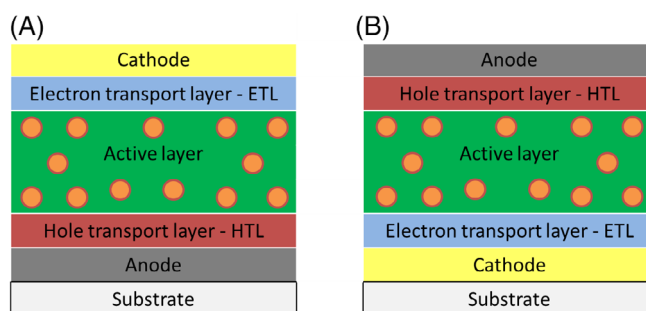


FIGURE 1 Schematic diagrams of, A, a conventional OPV and B, an inverted OPV [Colour figure can be viewed at wileyonlinelibrary.com]

substrate.³ Inkjet printing is an exception to this rule, as there is no direct contact between the stamp and the substrate. Inkjet printing is the only technique that can be classified in both categories (printing and coating) because even though it is essentially a coating technique, it has the possibility to reproduce a complex pattern, and its correlation with printing on paper allows it to be called as a technique that is also part of its name. Another feature of printing techniques is the two-dimensional pattern. Among the printing methods are gravure printing, flexographic printing, offset lithography printing, screen printing, inkjet printing, pad printing, and casting.^{7,9,11}

A complication with printing is the need for the electrode to flow during the manufacturing process. The use of metal deposited on plastic, mainly ITO in poly (ethylene terephthalate) (PET), is prone to cracking during bending and reduces the efficiency of the device. One of the main factors that limit the quality of the layers printed on OPV devices and, therefore, hinder the large-scale commercialization of OPV technologies is the lack of ink development protocols. An important part of the printing process is the ability to transfer ink from the printing plate to the target substrate. For the ink to be completely transferred from the plate to the substrate, the ink must be sufficiently fluid, with the required viscosity at the desired printing temperature. After the printing process, the solvent must evaporate in a controlled manner to leave a stabilized, homogeneous and conductive film.¹⁵

In the printing method, the choice of solvents for ink preparation was identified as an important parameter for the morphology of the deposited layer.¹¹

The main challenge for the manufacture of multilayer solar cells on flexible substrates is the optimization of the surface tension of the paint for the surface energy of the substrate and subsequent layers. Secondly, the viscosity of the ink must be adapted for printing: too high a viscosity leads to clogging of the scraper blade, too low a viscosity results in the incomplete transfer of ink to the device.¹⁵

2.1.1 | Gravure printing

Rotogravure printing, or direct engraving, consists of a two-roll system. The printing roller has an engraved pattern (small cavities), and as it is partially immersed in an ink reservoir, the cavities are being filled. Before the roller comes into contact with the screen, the excess ink is removed by the scraper blade. The coating roll is forced into the support roller (usually made of hard rubber) that guides the screen. The ink is transferred from the

engraving to the substrate in the desired pattern. When changing the pattern, a new roll has to be engraved, and this is an expensive process.^{7,9,14} An outline of the print-making technique is shown in Figure 2.

The nature of the ink directly influences the efficiency of printing. In this type of printing, the viscosity determines how the ink is transferred from the scraper blade to the substrate and how the ink spreads on the substrate to form a homogeneous film. If the viscosity of the ink is not adequate, printing will not occur as desired, due to the incomplete transfer of ink from the printing plate to the substrate.¹⁵ Thus, the control of print quality depends on the viscosity of the liquid polymer, which is influenced by the “temperature, pressure, molecular weight of the polymer, solvent, concentration, additives, and purity of the polymer itself.”^{15(p80)}

Rotogravure printing provides high quality, high-resolution printing, high speeds (1–10 ms^{−1}), and film thicknesses suitable for OPVs.^{7,14} Välimäki *et al.*¹⁶ processed the electron transport layer (ZnO) and the active layer (P3HT: PCBM) of inverted OPVs by printing prints. Yang *et al.*¹⁴ describe the use of an industrial gravure print developer to print the hole transport layer (PEDOT: PSS), the active layer (P3HT: PCBM) and the electron transport layer (ZnO).

Cho *et al.*¹⁷ prepared PEDOT:PSS as a transparent conductive anode (replacing the conventional ITO) by gravure printing. Voigt *et al.*¹⁵ developed inverted organic photovoltaic cells with the electron transport layer (TiO_x) and holes (PEDOT:PSS) and with the active layer (P3HT: PCBM) printed by gravure and analyzed the influence of

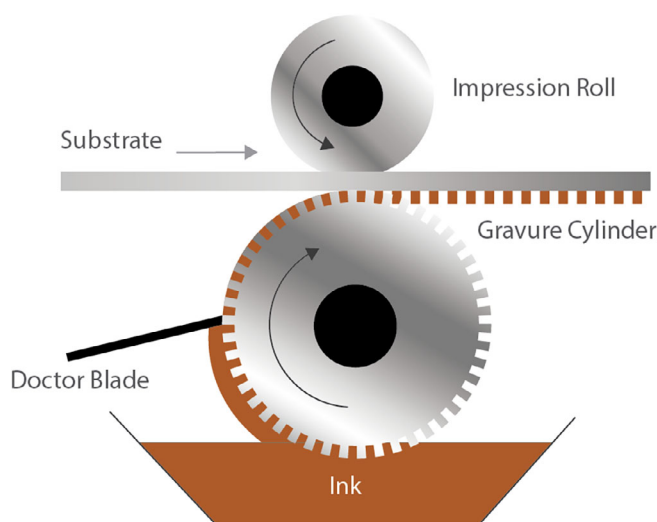


FIGURE 2 Illustration of the gravure printing process. Source: Adapted from Yang, Vak, Clark, Subbiah, Wong, Jones *et al.*¹⁴ and Aziz, Ismail¹¹ [Colour figure can be viewed at wileyonlinelibrary.com]

ink properties on the quality of the film and device performance. The studied device presented the following layer structure: PET/ITO/TiO_x/P3HT:PCBM/PEDOT:PSS/Au. The authors report that the choice of solvent can affect the morphology and, consequently, the performance of the device.

Schneider *et al.*¹⁸ studied the photovoltaic properties of a conventional OPV, with the structure ITO/PEDOT:PSS/PTB7:PCBM/Ca/Al, which the active layer PTB7:PCBM was printed by rotogravure. Välimäki *et al.*¹⁹ coated the active layer (P3HT:PCBM) and the layer (PEDOT:PSS) by the rotogravure method. Zhang *et al.*²⁰ processed thin films of large area ZnO as an electron transport layer. Wei *et al.*²¹ printed ZnO@APTMS nanoparticles as an electron transport layer on an inverted OPV. Wei *et al.*²² printed the electron transport layer ZnO:PEI. Li *et al.*²³ printed the P3HT:PCBM layer by gravure.

2.1.2 | Flexographic printing

Flexographic printing (Figure 3) consists of a fountain roller, which transfers the ink to the anilox roller, which is ceramic and has small cavities engraved on the outside. These cavities allow the ink to be collected and transferred to the printing cylinder, which is a photopolymer or a rubber plate on which the image is reproduced in relief. The printing cylinder then transfers the ink to the substrate.^{7,9,24}

The main difference between the flexographic process and rotogravure is that, in flexography, the transfer of ink is done through a relief opposite the cavities. Flexography can be used in the printing of different types of materials, as well as being a less expensive alternative than rotogravure due to the low cost of printing cylinders compared to engraving cylinders.^{7,9,24} However, both

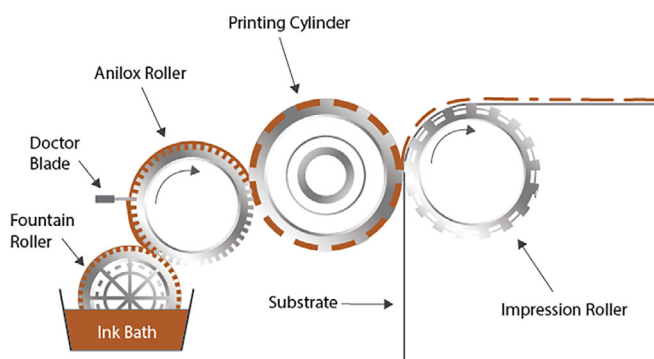


FIGURE 3 Illustration of the flexographic printing process. Source: Adapted from Krebs⁷ [Colour figure can be viewed at wileyonlinelibrary.com]

printing techniques have similar advantages over the slit matrix coating in terms of standardization and yield.²⁴

The use of flexographic printing on organic photovoltaic cells is recent.²⁵ Hösel *et al.*¹³ used, among other techniques, flexography in anode printing (silver bottom electrodes) for inverted organic solar cell modules. According to these authors, flexographic printing would be the best technique for manufacturing a silver electrode, as it has a high production speed ($>10 \text{ min}^{-1}$), consumes less ink, as ink waste can almost be avoided with ink control on the anilox roll.

Alem *et al.*²⁴ demonstrated a solar cell with the electron transport layer (ZnO) and the active layer (PCDTBT:PC71BM) deposited using flexography. The active layer processed by flexography was demonstrated by the manufacture of photovoltaic cells of 1 cm^2 that showed an efficiency of up to 3.5%, which is comparable to other printing/coating techniques. Hart *et al.*²⁶ printed the anode (Ag) using flexographic printing.

2.1.3 | Offset lithography

Lithography is based on two-dimensional printing where, unlike other techniques, the printed and unprinted areas are on the same plane. The offset lithography process is based on the incompatibility between water and fatty substances, so that the printed areas attract the greasy ink and repel water and the unprinted areas do the opposite. The inked image is then passed to a roller that transfers the impression to the substrate.^{7,27} Figure 4 shows the offset lithography printing process.

Offset lithography is a fast process and is a promising technique for printing OPVs. However, it will require

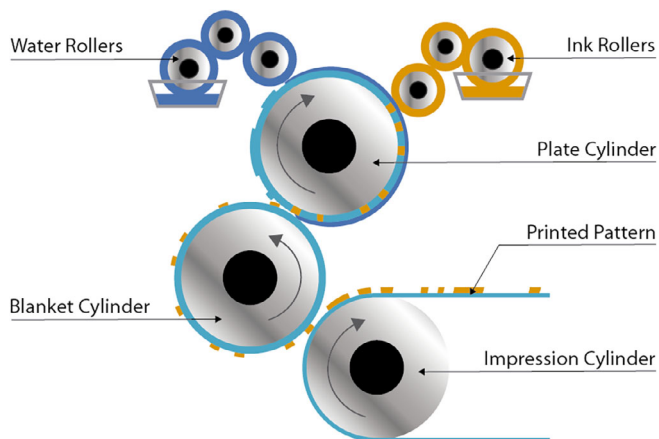


FIGURE 4 Illustration of the, A, front and B, side view of the offset printing process. Source: Adapted from Kipphan²⁷ [Colour figure can be viewed at wileyonlinelibrary.com]

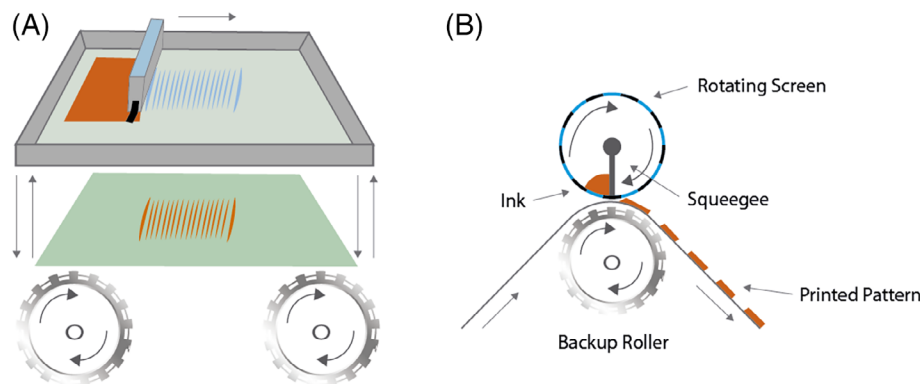


FIGURE 5 Illustration of the screen printing process. Source: Adapted from Søndergaard, Hösel, Krebs⁴ and Søndergaard, Hösel, Angmo, Larsen-Olsen, Krebs⁹ [Colour figure can be viewed at wileyonlinelibrary.com]

some development of ink systems before it can be used in organic photovoltaics.⁷

2.1.4 | Screen printing

Screen printing is a versatile technique, based on two-dimensional printing^{4,7,25,28} and considered economical, as there is no waste of coating solution during printing.³ There are two types of screen printing (flat and rotary),^{4,7,9,29} as illustrated in Figure 5.

In flat screen printing, the desired pattern is reproduced by the open areas of a screen, which are placed at a certain distance between the substrate, so that a squeegee moves in relation to the screen, forcing the ink through the screen openings for the substrate.^{4,7,9,13,25,29} The screen has a relatively low cost compared to the rotating screen and is, therefore, more suitable for laboratory work. In flat screen printing, it is possible to perform one print at a time and, making simple adjustments, it is possible to print different patterns over large areas.^{4,9}

Unlike the flat base, on rotary screen printing, the squeegee remains stationary and, just like the ink, is located inside the rotating screen.^{4,9,25} “As the screen rotates with the same speed as the substrate the ink is continuously pushed through the open area of the screen by the stationary squeegee, making a full print upon every rotation.”^{4(p18)} Regarding the processing speed, rotary screen printing reaches higher speeds (>100 m/min) than flat printing (0–35 m/min). However, due to limited access to the inside of the rotating screen, cleaning and adjustments are more difficult and time-consuming to perform.^{4,9,25}

The thickness of the wet layer of the printed film is defined by the thickness and the open area of the screen, and very thick damp layers (10–500 μm) can be obtained.^{7,13,25,28} “Some factors, however, are influential on this such that not all the material in the screen is deposited. This varies with the force with which the

squeegee is pushed into the screen, the snap-off distance, the speed of the squeegee and the viscosity of the solution.”^{7(p400)}

Both screen prints require high viscosity inks with a thixotropic behavior, as inks with lower viscosities will pass straight through the screen openings.^{4,7,9,13,25,29} Another important aspect to be taken into account is the volatility of the solvent because if very volatile solvents are used, they will dry out on the screen printing mask damaging the definition of the printed pattern.^{7,25,28}

Krebs *et al.*³⁰ used screen printing in donor training (MEH-PPV) and demonstrated the feasibility of this technique in an industrial environment and claim to be a cheap, fast technique (cells can be printed in 20s for each printing operation) and reliable to produce OPVs. Krebs *et al.*²⁸ manufactured inverted OPVs using screen printing to print the anode (Ag), the active layers (P3CT:PCBM/ZnO and P3CT:ZnO) and the hole transport layers (PEDOT:PSS) and electron (ZnO).

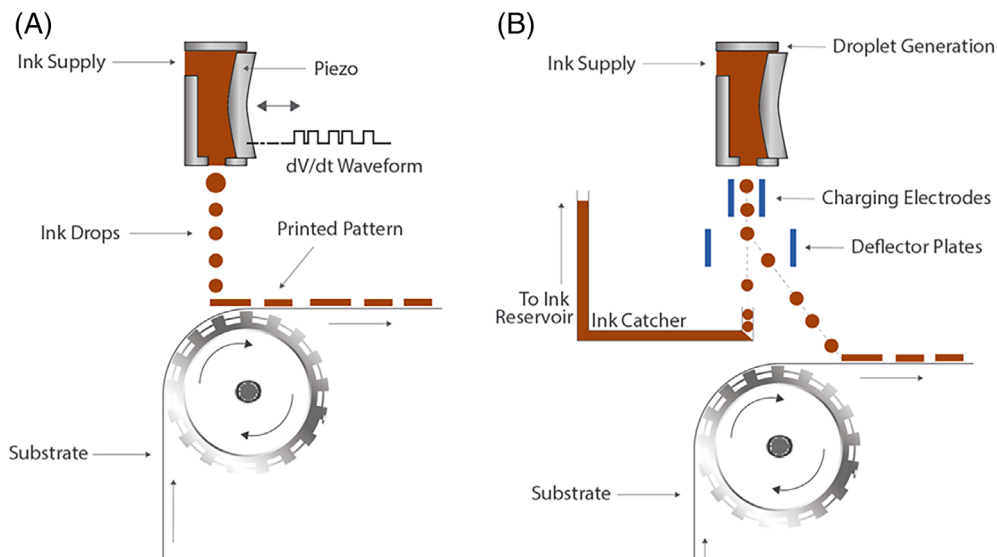
Krebs³¹ prepared the hole transport layer (PEDOT:PSS) and the anode (Ag) using screen printing. Välimäki *et al.*¹⁶ used rotary screen printing to process the cathode (ITO), the hole transport layer (PEDOT:PSS), and the anode (Ag) of an inverted OPV. Angmo *et al.*³² printed the AgNW/ZnO layer using rotary screen printing. Pali *et al.*³³ used screen printing to print PEDOT:PSS as anode.

2.1.5 | Inkjet printing

Inkjet printing is a two-dimensional technique that consists of expelling fixed amounts of ink droplets through the nozzles. The manner in which droplets are formed varies according to the different inkjet systems.³⁴ Figure 6 illustrates the continuous and on-demand inkjet printing.

In continuous printing, ink droplets are generated and expelled continuously through a small nozzle, which is placed at a distance from the substrate. When going toward the substrate, with the help of gravity, the

FIGURE 6 Illustration of the, A, continuous inkjet printing process and B, on-demand inkjet printing. Source: Adapted from Søndergaard, Hösel, Angmo, Larsen-Olsen, Krebs⁹ [Colour figure can be viewed at wileyonlinelibrary.com]



droplets pass through the charging electrodes, where they receive a small charge, and through the deflection plates, which direct these droplets to the stationary or mobile substrate.^{9,34} “A piezoelectric transducer is often used to subject the liquid behind the nozzle to a small pressure fluctuation, which is used to synchronize droplet formation.”^{34(p2)}

In print on-demand, ink droplets are generated and expelled on demand, thus providing ink savings. The generation of a pressure pulse taunting the volume of the ink reservoir to change, causing the ink is ejected through the print nozzles. The pressure pulse can be generated by the thermal method or by the piezoelectric method. In the thermal method, the heating of the ink caused by a resistive element located in the ink reservoir causes bubbles of steam to be formed, expanded, and collapsed, then directing the inkjet out of the nozzles. In the piezoelectric method, the pulse is generated by the mechanical deformation of a piezoelectric transducer (PZT) due to the application of an electric field.^{4,9,34}

A barrier to the use of inkjet printing is the fact that this technique is unable to achieve high printing speeds.⁷ However, due to its versatility and flexibility, it has the potential to be increasingly used in the manufacture of OPVs.^{34,35}

Inkjet printing was also used by Eom *et al.*³⁶ when printing the cathode (Ag). Eom *et al.*³⁷ produced an OPV with PCE of 3.71% through inkjet printing of the hole transport layers (PEDOT:PSS) and active (P3HT:PCBM) with additives. The authors found that the device's performance was strongly influenced by the addition of high boiling point additives to the photoactive ink with chlorobenzene solvent.

Eggenhuisen *et al.*³⁵ fabricated by inkjet printing, using nonhalogenated solvents, the electron transport

layers (PEDOT/ZnO) and holes (PEDOT:PSS) and the active layer (P3HT: PCBM) of an inverted OPV. Lu *et al.*³⁸ used inkjet printing for anode printing (AgNWs). Sankaran *et al.*³⁹ printed the active layer (P3HT:IC[60] BA), the electron transport layers (ZnO) and holes (PEDOT:PSS), resulting in a cell with PCE of 2.9%. Maisch *et al.*⁴⁰ printed the cathode (AgNWs) and anode (AgNWs) by means of inkjet printing obtaining OPV with PCE of 4.3% for an area of 1 cm². Ganesan *et al.*⁴⁰ printed the active layer (P3HT:ICBA) and the electron transport layer (ZnO).

2.1.6 | Pad printing

Pad printing is a two-dimensional technique, which uses a silicone rubber stamp to transfer the pattern of an engraving to the substrate,^{7,25,42} see Figure 7.

As shown in Figure 7, the pad printing process comprises six steps. Initially, the ink cup (which allows the use of relatively volatile solvents) and the pad (stamp) is moved to the left, leaving exposed the gravure, which is full of ink. In step two, the pad is pressed over the printing pattern, and the ink is collected. Then the ink cup and the pad are moved to the right, so that the ink cartridge refills the gravure, and the pad is placed above the substrate. In the fourth step, the pad is pressed onto the substrate, and the desired pattern is printed. After printing, the substrate is removed (fifth step), and then replaced, leaving the printer ready to start a new print (sixth step).⁴²

Pad printing is used for printing on substrates that have irregular surfaces, such curvatures surfaces convex and concave. However, this method is still not widely used, as it is only suitable for printing small areas, as well

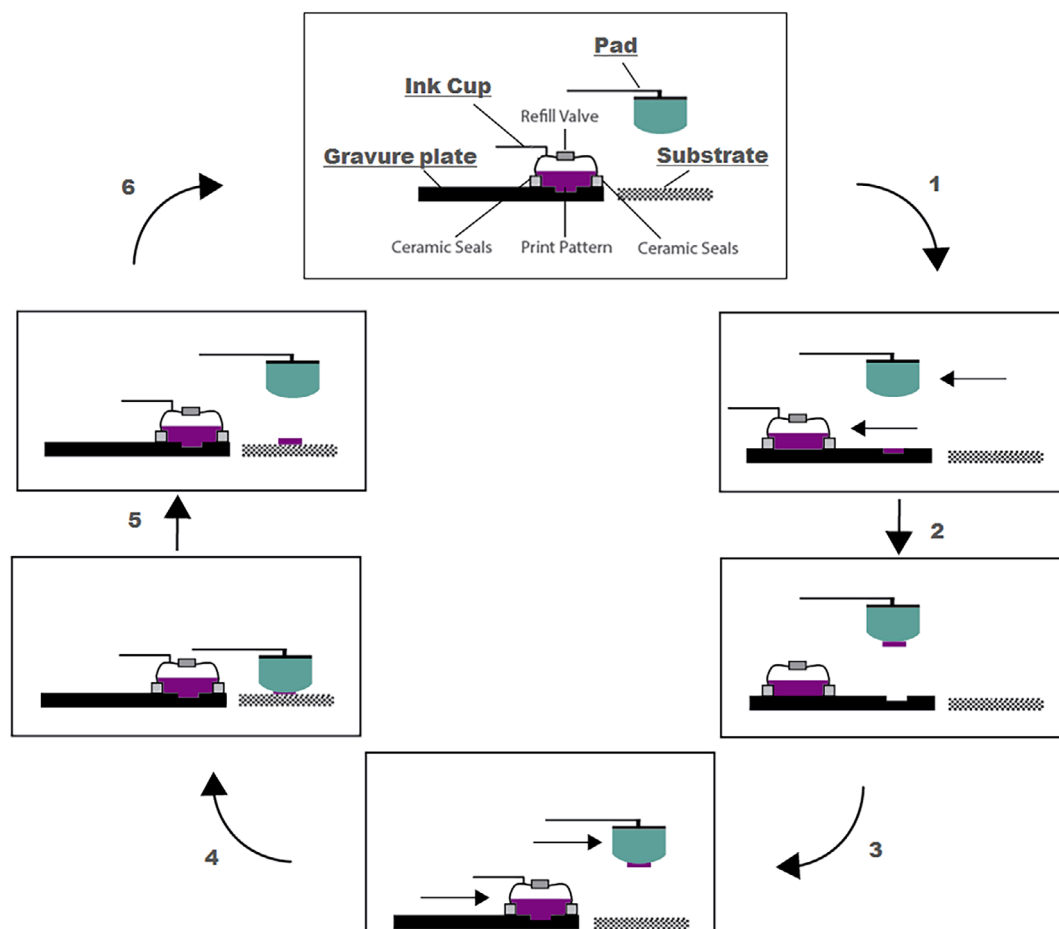


FIGURE 7 Illustration of the pad printing process. Source: Adapted from Krebs,⁷ Wang, Adil, Zhang, Wei,¹⁷ and Krebs⁴² [Colour figure can be viewed at wileyonlinelibrary.com]

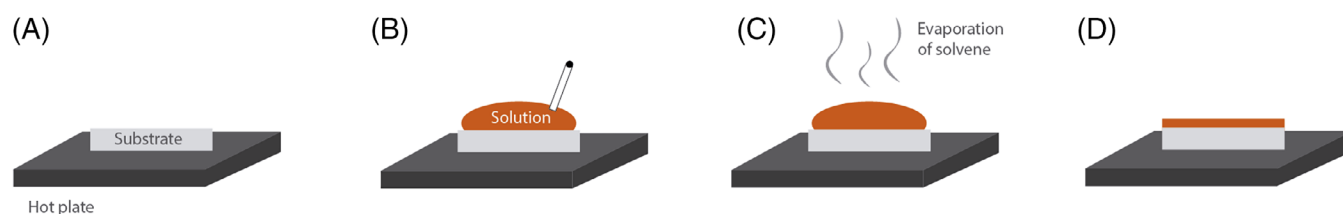


FIGURE 8 Illustration of the casting process [Colour figure can be viewed at wileyonlinelibrary.com]

as being a parsimonious method, that is, a relatively large volume of ink is required to perform the printing and ink acquisition is not easy.^{7,25} Has been demonstrated pad printing to prepare the active layer P3CT-ZnO in⁴²

2.1.7 | Casting

The casting method (Figure 8) is a print technique of dimension 0 and is an essentially manual method. Initially, the substrate is placed on a horizontal work surface (a) then a polymeric solution is deposited on the

substrate (b). Subsequently, the solvent contained in the solution evaporates (c), that is, the solution is dried, resulting in a thin film (d).⁷

This printing method allows for depositing of good quality films and thick films. However, in this technique, it is not possible to control the thickness of the film, and “often picture framing effects are observed near the edges of the film or precipitation during drying. In cases where the surface tension of the liquid dominates the drying is inhomogeneous.”^{7(p398)} Dai *et al.*⁴³ demonstrated to be useful the formation of the active layer (P3HT:PCBM) by the casting process.

2.2 | Coating techniques

The coating consists of transferring a layer of ink to the substrate.⁷ Coating techniques include spin coating, meniscus, slot die, knife-over-edge coating-blade coating-doctor blading, spray, brush, curtain, slide, and multiple slot die coating.

2.2.1 | Spin coating

The spin coating (Figure 9) is a coating technique of dimension 0, which consists of depositing an amount of liquid over the flat substrate and submitting the substrate to a centrifugal force, rotating it from 1000 to 5000 rpm (rpm), so that the liquid is spread. Another deposition option is to apply the liquid while the substrate is rotating. As the centrifugation occurs, the solvent, which is normally volatile, evaporates and dilutes the film until the final thickness (from 100 to 200 nm) is obtained.^{7,44,45} The film thickness is controlled empirically, “As there is no linear relationship between film thickness and coating parameters (such as spin speed, acceleration, coating time, and solution concentration).”^{45(p033302-1)}

Spin coating, due to its simplicity of use, is the most widely used laboratory technique to manufacture small and uniform thin film OPVs. However, this application method is not suitable for processing OPV modules for large areas at high rates, as it has some inherent limitations, such as the loss of a large amount of material during coating and limited control over the thickness of the film. Despite being a less expensive technology, the loss of a large amount of solution makes this technique

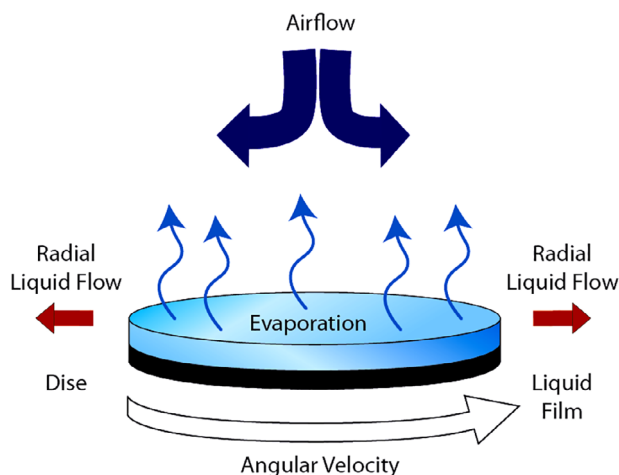


FIGURE 9 Illustration of the spin coating process. Source: Adapted from Krebs⁷ [Colour figure can be viewed at wileyonlinelibrary.com]

incompatible with the promising large-scale roll-to-roll.^{3,7,8,11,14,45-47}

Spin coating was used to form the donor G-P3HT in as mentioned the study⁴⁸ and the active layers P3HT:PCBM in the studies,^{17,36,45,49-65} P3HT:MIF in the study,⁶² P3HS:PCBM in the study,⁶⁶ PTB7:PCBM in the study,⁶⁷ PTB7:PC₇₀BM in the study,⁶⁸ PTB7:PC₇₁BM and PTB7-Th:PC₇₁BM in the study,⁶⁹ PBDB-T-SF:IT-4F in the study,⁷⁰ PBDB-T:PC₇₁BM in the study,⁷¹ PBDB-TSR:PC₇₁BM in the study,⁷² PBDB-T:ITC in the study,⁷³ PTB7-Th:PC₇₁BM in the study,⁷⁴ P3HT:ICBA in the studies,^{39,75-77} PTB7:PC₇₁BM:P-GO in the study,⁷⁸ MEH-PPV:PCBM in the study,⁷⁹ ZnPc-TB:PTCBI in the study,⁸⁰ PEHBDT-DFDTBSe:PC₇₁BM in the study,⁷⁵ PBDTTT-C:PCBM in the study,⁸¹ PBDTT-F-TT:diPBI in the study,⁸² PBDB-T:FH, PBDB-T:FM, PTB7-Th:NFBTD, and PTB7-Th:NOBDT in the study,⁸³ PSBTBT:PDI-DTT in the study,⁸⁴ PDBT-T1:SdiPBI-S in the study,⁸⁵ PBDT-8:PC₇₁BM and PTIPSBDT-DFDTQX:PC₇₁BM in the study⁸⁶ and PBDT-TSR:PC₇₁BM in the study.⁷²

Spin coating was also used to process the PEDOT:PSS hole transport layers as mentioned in the studies,^{36,39,42,45,49,51,52,54,56-60,66,68,72,75-77,82-84,86-96} Au@SiO₂-WO₃ in the study,⁶⁵ GO/NiO_x in the study,⁹⁷ PDPA-GO in the study,⁷⁶ of the AgNWs cathode in an inverted OPV in the studies,^{52,60} of the electron transport layers NaCl:MeOH in the study,⁶³ CNTs-TiO_x in the study,⁵⁵ FTO/PEIE in the study,⁸¹ PEIE in the studies,^{75,81,86} and ZnO in the studies.^{36,39,42,55,61,64,68,71,72,74,82,83}

2.2.2 | Meniscus coating

The meniscus coating (Figure 10) is a coating technique of dimension 0,⁷ where the paint is pumped into the applicator roller, which has pores, is made of stainless steel, and can rotate in the same direction or in the opposite direction that the substrate. The paint passes through the porous wall of the applicator roll, forming a film on the substrate, which is moved by the coating roller, which is some distance from the applicator roll. The meniscus formed in the space between the two rollers depends on the distance between the rollers, as well as the speed and direction of the roll.^{7,43,98-101}

With the meniscus coating, it is possible to process ultra-thin, high-quality films,⁹⁸ and in comparison with the rotating coating, it is able to process large area OPVs with little ink waste, which favors the cost reduction of this technique.¹⁰⁰

Ghoos *et al.*¹⁰¹ deposited the active layer P3(mim)HT-TFSI:PCBM through the meniscus coating and showed that the modified polymer P3(mim)HT-TFSI performed at or above the standard P3HT in a two-layer

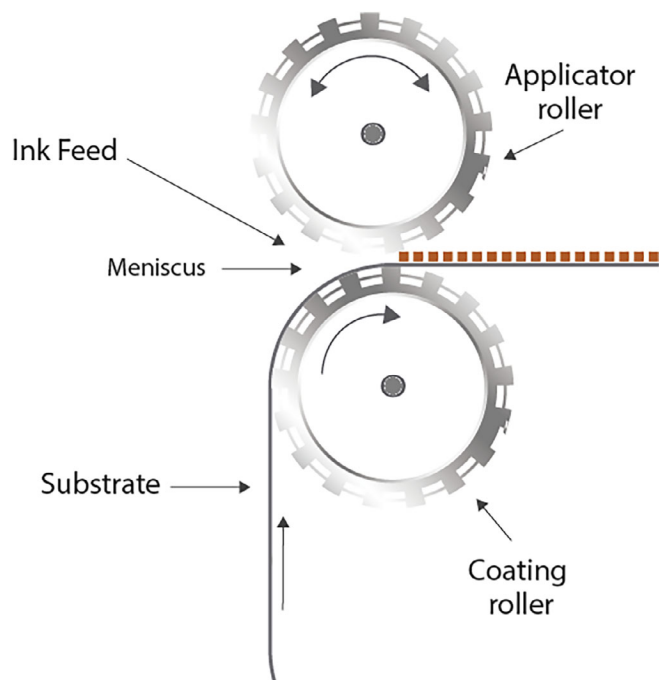


FIGURE 10 Illustration of the meniscus coating process. Source: Adapted from Krebs⁷ [Colour figure can be viewed at wileyonlinelibrary.com]

configuration. Shaw *et al.*¹⁰² investigated the microstructural evolution of thin films of a polymer semiconductor with the PDPP3T donor deposited by meniscus coating.

2.2.3 | Slot die coating

Slot die coating (Figure 11) is a one-dimensional coating technique, without loss of paint, which can be used to coat one or more layers, as well as be transferred to a large area process with reproducibility on an industrial scale. It is considered a laboratory scale version of the R2R fabrication. In this technique, the paint is directly coated on the substrate by means of a stainless steel coating head. The ink is fed and flows through the coating head at a defined flow, and the substrate is moved perpendicularly under it. The ink reaches the meniscus by means of a pump or pressure system. The speed with which the substrate moves and the amount of ink deposited determines the thickness of the film.^{4,7,9,25,43,103-105}

Slot die coating was used to process the hole transport layer (PEDOT:PSS) in the studies,^{8,26,31,106-108} the active layer (P3HT:PCBM) in the studies,^{8,103,106,108,109} the electron transport layer (ZnO) in the studies,^{8,106} the active layer (P3CT/ZnO) in the study³¹ and the anode (Ag) in the studies.^{31,106} Zhao *et al.*¹⁰⁵ manufactured an OPV, with 12.5% PCE, with the active layer PBDB-T:i-IEICO-

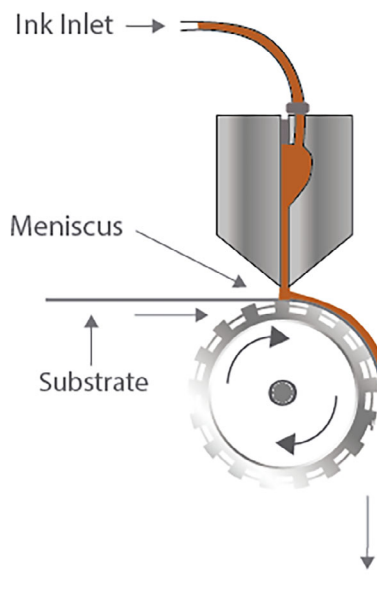


FIGURE 11 Illustration of the slot die coating process. Source: Adapted from Søndergaard, Hösel, Krebs⁴ and Søndergaard, Hösel, Angmo, Larsen-Olsen, Krebs⁹ [Colour figure can be viewed at wileyonlinelibrary.com]

4F processed by slit matrix coating. To prove that the slit matrix coating can be used in the R2R fabrication of large area modules, and that it is possible to decrease the distance between the efficiency of laboratory-produced and industrial-scale OPVs, Lee *et al.*¹¹⁰ processed the active layer (PTB7-Th:PC71BM:COi8DFIC) of a ternary single-junction OPV with high PCE (13.5%) and Wu *et al.*¹⁰ coated the PBDB-T-SF:IT-4F active layer of an OPV with 12.90% PCE.

2.2.4 | Knife-over-edge coating—blade coating—doctor blading

The knife coating (R2R on a large scale), also called blade coating (laboratory scale), see Figure 12, is a zero dimension method used in the processing of large areas with no defined pattern and without wasting ink during coating.^{4,7,9,12}

In the large-scale R2R process, the knife is stationary, and the substrate is the one that moves, while in a laboratory scale, the knife is mobile, and the substrate is fixed. The ink is deposited before the knife, which is positioned parallel to the direction of movement of the substrate, removing excess ink and forming a coating layer when the substrate moves at a specific speed.^{4,7,9,25} The amount of ink transferred to the substrate can be controlled manually, “Thus ensuring that only a small amount of ink is

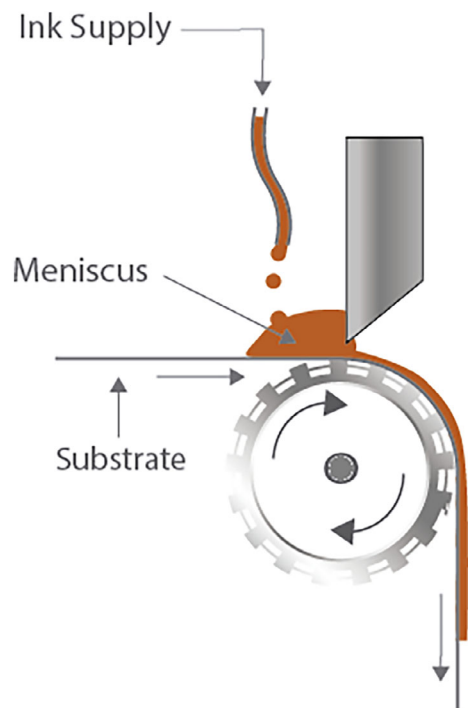


FIGURE 12 Illustration of the knife-edge coating process. Source: Adapted from Søndergaard, Hösel, Krebs⁴ and Søndergaard, Hösel, Angmo, Larsen-Olsen, Krebs⁹ [Colour figure can be viewed at wileyonlinelibrary.com]

in front of the knife and avoiding that it runs down over the roller. Alternatively, a small piston pump may be employed to maintain a sufficient flow of liquid in the front of the knife.^{7(p404)}

The thickness of the coated layer is approximately half the space between the knife and the substrate and is influenced by the speed of the coating, size of the gap between the knife and the substrate, concentration of solids in the paint, density of the material in the final film.^{4,7,9,12,25}

The use of knife-over-edge coating has been reported in the manufacture of the electron transport layer ZnO in Reference 31 and the active layer P3HT:PCBM in References 103,111. The blade coating was used in the preparation of the active layers P3HT:PCBM mentioned in the studies,^{89,90,111} PBDB-TSR:PC71BM in the study⁷² and PBTA-TF:ITCC, PBTA-TF:IT-M, PBTA-TF:IT-4F in the study,¹¹² PBDB-T:ITC in the study,⁷³ the ZnO electron transport layer in the study¹¹³ and PEDOT:PSS hole transport layers in the study.⁹⁶

Schneider *et al.*¹⁸ in addition to printing the active layer PTB7:PCBM by rotogravure, they also did it using blade coating. Guo *et al.*¹¹⁴ used the blade coating to manufacture all layers of an OPV with the structure AgNW/PEDOT:PSS/pDPP5T-2:PCBM/ZnO/AgNW. All layers of a tandem OPV (Ag/PEDOT:PSS/GEN-2:PCBM/ZnO/N-PEDOT/pDPP5T-2:PCBM/ZnO/AgNWs) were processed using the blade coating in Guo *et al.*¹¹⁵

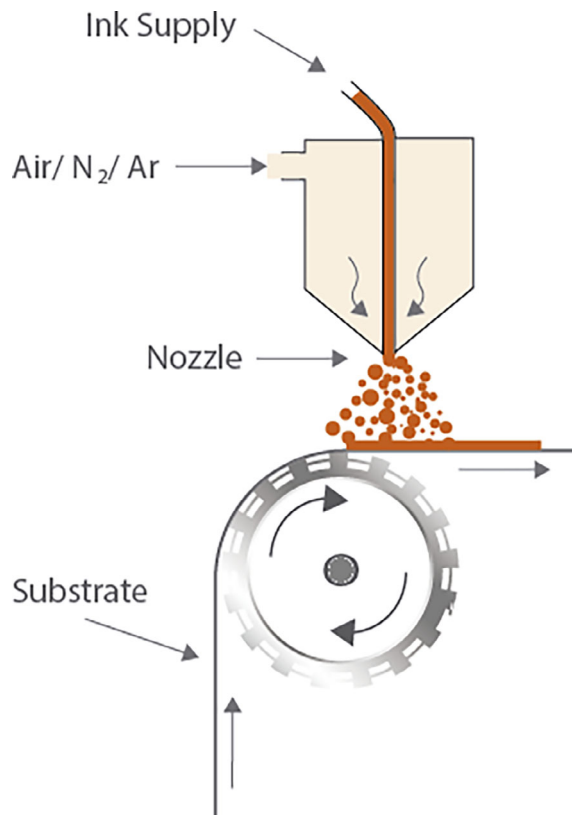


FIGURE 13 Illustration of the spray coating process. Source: Adapted from Søndergaard, Hösel, Krebs⁴ and Søndergaard, Hösel, Angmo, Larsen-Olsen, Krebs⁹ [Colour figure can be viewed at wileyonlinelibrary.com]

Sankaran, Glaser, Gartner, Rodlmier, Sudau, Sosa *et al.*,³⁹ in addition to printing with inkjet and by spin coating the active layer P3HT:IC[60]BA, the layers of electron transport ZnO and holes PEDOT:PSS, also did it by blade coating. Ji *et al.*¹¹⁶ manufactured an inverted OPV (ITO/ZnO/PBDB-TF:IT-4F/MoO₃/Al) with 12.88% PCE, where the electron transport layer (ZnO) was processed through the blade coating.

2.2.5 | Spray coating

Spray coating (Figure 13) is a zero-dimension, noncontact coating technique,^{4,9,25} where a continuous spray of paint is atomized into a spray nozzle. Pneumatically driven spraying uses a stream of air or pressurized gas (eg, nitrogen or argon) that breaks down paint into droplets in the nozzle and helps direct the aerosol to reach the substrate. The atomization process is influenced by the surface tension, viscosity and density of the paint, gas flow properties, and size and shape of the nozzle.^{4,7,25,45}

The quality of the deposited layer is influenced by the distance between the nozzle and the substrate, coating

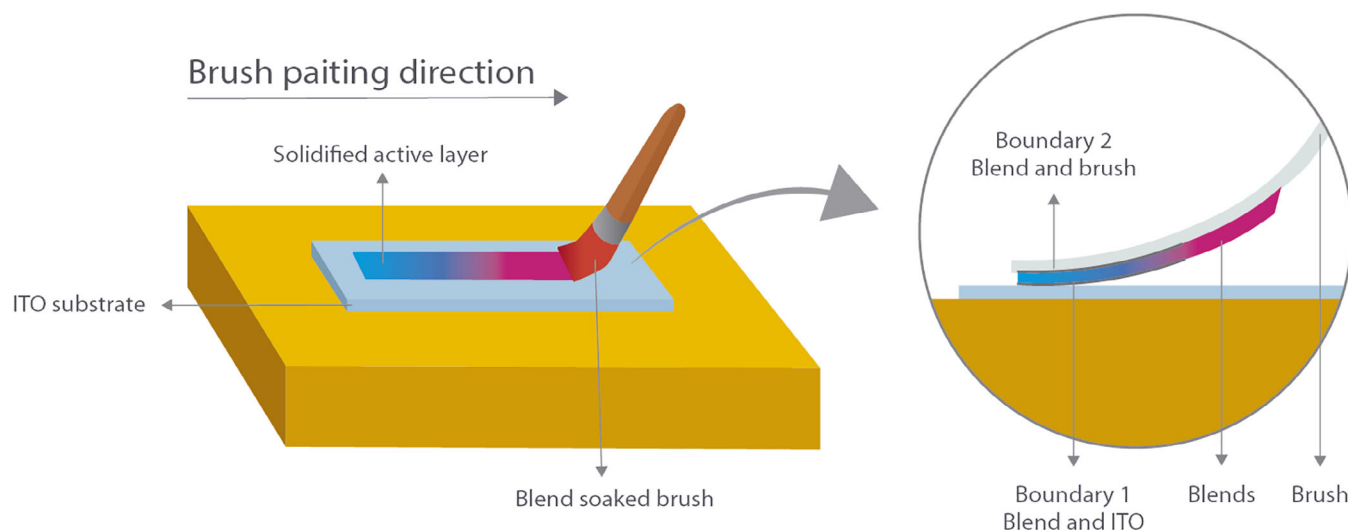


FIGURE 14 Illustration of the brush coating process. Source: Adapted from Wang, Adil, Zhang,²⁵ Wei and Kim, Na, Jo, Tae, Kim⁸⁸ [Colour figure can be viewed at wileyonlinelibrary.com]

speed, amount of sprayed paint, air or gas pressure, amount of coated layers, solvent used, substrate temperature, and phase evaporation control, by means of heating of substrate or mixed solvents.^{4,11,25}

Regarding the distance between the nozzle and the substrate, if the distance is large, the solvent will evaporate along the way to the substrate, causing a dry film. On the other hand, if the distance is small, the film will be moist and with holes.^{11,117,118} Thus, in order to obtain a homogeneous and without holes film, one must “To choose a fast drying solvent to prevent droplets from redissolving sublayers but not so fast so as to allow for a homogenous and pin-hole free film to form.”¹¹⁹

Spray coating has been used in several reports in the literature to prepare many of the layers OPV, including the active layer P3HT:PCBM in References 56,91,117,119,120, P3HT:ICBA in Reference 113, PFB: F8BT in Reference 118, PffBBT4T:PC70BM in Reference 95, of the AgNWs anode in References 113,121, hole transport layer PEDOT:PSS in References 96,113,117, and electron transport layer ZnO in References 95,117, and V₂O₅ in Reference 95.

Vak *et al.*⁴⁵ used the spray coating in the deposition of the active layer (P3HT:PCBM) and stated that this technique provides control of the film thickness similar to the control done in vacuum deposition.

2.2.6 | Brush coating

Brush coating (Figure 14) is a two-dimensional contact technique, compatible with roll-to-roll processing and can be used even on substrates with uneven surfaces. The

coating process consists of dipping the brush in the synthesized paint solution and then applying it to the heated substrate. The temperature adjustment of the substrate is a function to the evaporation rate of the solvent used. A fibrous paint brush is used to coat the substrates, which is usually made of nylon. The choice of nylon fibers is due to the fact that nylon does not dissolve in the paint solvent. The coated pattern depends on the brush size.^{9,25} This technique presents “low materials loss, high-speed fabrication, relatively better control of the film thickness due to faster film solidification rates.”^{25(p25)}

Kim *et al.*⁸⁸ used a nylon brush to deposit the active layer (P3HT:PCBM) of an OPV and concluded that this is a simple, low-cost and promising technique for the production of large areas on a large scale. The brush coating was applied to the coating of the AgNWs anode in the studies,^{54,122} CNT in the studies,⁵⁸ of the PEDOT:PSS hole transport layer in the study,¹²² of the active layer P3HT:PCBM in the studies,^{88,122,123} of the ZnO electron transport layer.¹²²

2.2.7 | Simultaneous coating techniques of many layers

Curtain coating (Figure 15A), slide coating (Figure 15B), and multiple slot die coating (Figure 15C) allow the simultaneous coating of several OPV layers (>10). These techniques have the potential to be the most important in the OPV scenario.^{7,9}

In order for curtain coating and slide coating techniques to be efficient in the processing of thin films, very fast ink flow and consequently a higher coating speed are required.⁷

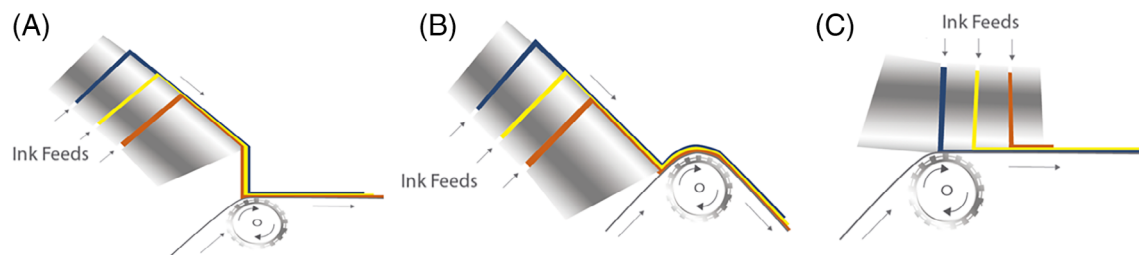


FIGURE 15 Illustration of the, A, curtain coating process; B, slide coating, and C, multiple slot die coating. Source: Adapted from Krebs⁷ and Søndergaard, Hösel, Angmo, Larsen-Olsen, Krebs⁹ [Colour figure can be viewed at wileyonlinelibrary.com]

Among these three simultaneous multi-layer coating techniques, double slot die coating was the only technique used in a complete R2R process.^{4,9} Andersen *et al.*¹⁰⁸ used a double slot die coating with aqueous inks for the simultaneous coating of the active layer (P3HT:PCBM) and the hole transport layer (PEDOT:PSS). In the double slot die coating, much lower web speeds are possible and on much smaller scale than the curtain and blade coating, and also allows for a much simpler control of the paint flow.^{4,7,9}

2.3 | Comparison of coating and printing techniques

Many coating and printing techniques that can be used in OPV processing have been introduced. With that, a summary table (Table 1) was elaborated to compare these techniques in relation to the processed layer, whether the technique is compatible with the R2R fabrication, dimension, and whether the technique is a contact technique or not.

According to Table 1, not all techniques are compatible with R2R processing, the printing techniques have a two-dimensional pattern, the coating techniques have a predominance of zero dimension, and among the printing techniques, only the jet printing of ink has no physical contact between the object carrying the motif and the substrate.

3 | CONCLUSION AND OUTLOOK

While it is possible to think about producing all layers of the OPV device using a single film-forming technique, it is more likely that the solar cell will be manufactured using a range of printing and coating techniques. Therefore, this article provided an overview of coating and printing techniques in the production of organic photovoltaic cells, that is, it characterized and compared the

most relevant coating and printing techniques that can be used in the manufacture of OPVs.

To develop high-throughput manufacturing processes, several approaches have been explored to manufacture medium and large area devices under environmental conditions, while preserving acceptable energy conversion efficiency.

The results indicate that the most used method for processing organic photovoltaic cells is spin coating since it requires only a few formulation efforts and homogeneous films can be manufactured with high reproducibility. However, the substrate size restriction and incompatibility with continuous processing do not establish it as a mass production method. Thus, one of the challenges of organic photovoltaics to be faced is the transfer of the laboratory scale to industrial applications. In the studies found, rotation was used to coat the active layer, the electron transport layer, and the hole transport layer.

The techniques of pad printing, casting, and meniscus are considered useful in the processing of the active layer. Regarding the deposition of the active layer, hole transport layer, electron transport layer and anode, the rotogravure, crack matrix, spraying, and brushing techniques were satisfactory. Flexography has been used to form the active layer, electron transport layer, and anode. Screen printing, inkjet printing, and knife/blade coating were used in the processing of the active layer, hole transport layer, electron transport layer, anode, and cathode. All the double slot die coating, curtain coating, and slide coating allows simultaneous processing of multiple layers.

Despite the difficulty in identifying, among the reviewed techniques, which will be successful in the field of organic photovoltaic technology, it can be said that roll-to-roll processing will be at the center of OPVs in the future. R2R printing and coating technologies have the potential to make organic photovoltaic technology more competitive. For this, closer cooperation between scientists and engineers is necessary to carry out the large-

TABLE 1 Comparison of coating and printing techniques

Technician	R2R compatible	Dimension	Contact	Material	Processed layer	References
Gravure printing	Yes	2	Yes	P3HT:PCBM	Active layer (donor + acceptor)	14-16,19,23
				PTB7:PCBM	Active layer (donor + acceptor)	18
				PEDOT:PSS	HTL	14,15,17,19
				ZnO	ETL	14,16,20
				ZnO@APTMS	ETL	21
				TiOx	ETL	15
Flexographic printing	Yes	2	Yes	ZnO:PEI	ETL	22
				PEDOT:PSS	Anode	17
				PCDTBT:PC71BM	Active layer (donor + acceptor)	24
				ZnO	ETL	24
				Ag	Anode	13,26
				—	—	—
Offset printing	Yes	2	Yes	—	—	—
Screen printing	Yes	2	Yes	MEH-PPV	Active layer (donor)	30
				P3CT:PCBM/ZnO	Active layer (donor + acceptor)	28
				P3CT/ZnO	Active layer (donor - doped with ZnO)	28
				PEDOT:PSS	HTL	16,28,31
				ZnO	ETL	28
				Ag	Anode	16,28,31
				PEDOT:PSS	Anode	33
				ITO	Cathode	16
				P3HT:ICBA	Active layer (donor + acceptor)	39,41
				P3HT:PCBM	Active layer (donor + acceptor)	35,41
Ink jet printing	Yes	2	No	PEDOT:PSS	HTL	35,37,39
				PEDOT/ZnO	ETL	35
				ZnO	ETL	39,41
				Ag	Cathode	36
				AgNWs	Anode	38
				AgNWs	Cathode	40
				—	—	—
				—	—	—

TABLE 1 (Continued)

Technician	R2R compatible	Dimension	Contact	Material	Processed layer	References
Pad printing	Yes	2	Yes	P3CT-ZnO	Active layer (donor - doped with ZnO)	42
Casting	No	0	No	P3HT:PCBM	Active layer (donor + acceptor)	43
Spin coating	No		No	G-P3HT	Active layer (donor - doped with graphene)	48
				PTB7:PCBM	Active layer (donor + acceptor)	67
				PTB7:PC70BM	Active layer (donor + acceptor)	68
				PTB7:PC71BM	Active layer (donor + acceptor)	69
				PTB7-Th:PC71BM	Active layer (donor + acceptor)	69
				PTB7:PC71BM:P-GO	Active layer (donor + acceptor - doped with graphene oxide)	78
				PTB7-Th:NFBTD	Active layer (donor + acceptor non fullerene)	83
				PBPT-8:PC71BM	Active layer (donor + acceptor)	86
				PTIPSBTD-DFDQX:PC71BM	Active layer (donor - copolymer + acceptor)	86
				P3HT:PCBM	Active layer (donor + acceptor)	17,36,49-51,53-55,58,59,61,62,64-66,88,91
				P3HT:ICBA	Active layer (donor + acceptor)	39
				P3HT:MIF	Active layer (donor + acceptor)	62
				MEH-PPV:PCBM	Active layer (donor + acceptor)	79
				PBDTTT-C:PCBM	Active layer (donor + acceptor)	81
				PBDTT-F-TT:diPBI	Active layer (donor + acceptor)	82
				PBDB-T:FH	Active layer (donor + acceptor non fullerene)	83
				PBDB-T:FM	Active layer (donor + acceptor non fullerene)	83
				PBDT-TSR:PC71BM	Active layer (donor + acceptor)	72
				ZnPcTB:PTCBI	Active layer (donor + acceptor)	80
				P3HT:ICBA	Active layer (donor + acceptor)	75,77
				PEHBDT-DFDQX:PC71BM	Active layer (donor - copolymer + acceptor)	75

(Continues)

TABLE 1 (Continued)

Technician	R2R compatible	Dimension	Contact	Material	Processed layer	References
Meniscus coating	Yes	0	No	PSBTBT:PDI-DTT	Active layer (donor + acceptor – both polymer)	84
				PDBT-T1:SdiPBI-S	Active layer (donor + acceptor non fullerene)	85
				PEDOT:PSS	HTL	36,39,42,45,49,51,54,56,58,59,62,66,68,72,75-77,82-84,86-96
				GO/NiO _x	HTL	97
				Au@SiO ₂ -WO ₃	HTL	65
				PDDA-GO	HTL	76
				ZnO	ETL	36,39,42,61,64,72,73,82,83
				CNTs-TiO _x	ETL	55
				PEIE	ETL	73,79,84
				PDP3T	Active layer (donor)	102
Slot die coating	Yes	1	No	P3(mim)HT:TFSI:PCBM	Active layer (donor + acceptor)	101
				P3HT:PCBM	Active layer (donor + acceptor)	8,103,106,108,109
				PTB7-Th:PC71BM:COi8DFIC	Active layer (donor + acceptor + acceptor)	10
				PBDB-T:i-IEICO-4F	Active layer (donor + acceptor non fullerene)	105
				PBDB-T-SF:IT-4F	Active layer (donor + acceptor non fullerene)	10
				P3CT/ZnO	Active layer (donor - doped with ZnO)	31
				PEDOT:PSS	HTL	8,26,89,106-108
				ZnO	ETL	8,106
				Ag	Anode	31
				P3HT:PCBM	Active layer (donor + acceptor)	89,90,111
Knife-Over-Edge coating/ Blade coating	Yes	0	No	P3HT:ICBA	Active layer (donor + acceptor)	39
				PBT-TSR:PC71BM	Active layer (donor + acceptor)	72
				PBTA-TF:ITCC	Active layer (donor + acceptor non fullerene)	112
				PBTA-TF:IT-M	Active layer (donor + acceptor non fullerene)	112

TABLE 1 (Continued)

Technician	R2R compatible	Dimension	Contact	Material	Processed layer	References
Spray coating	Yes	0	No	PBTA-TF:IT-4F	Active layer (donor + acceptor non fullerene)	112
				PTB7:PCBM	Active layer (donor + acceptor)	18
				pDPP5T-2:PCBM	Active layer (donor + acceptor)	114
				PEDOT:PSS	HTL	39,62,96,114
				ZnO	ETL	31,39,73,111,113,114,116
				AgNWs	Cathode	114
				AgNWs	Anode	114
				P3HT:PCBM	Active layer (donor + acceptor)	45,56,91,117,119,120
				P3HT:ICBA	Active layer (donor + acceptor)	113
				PFB:F8BT	Active layer (donor + acceptor – both polymer)	118
Brush Coating	More or less	2	Yes	PfBBT4T:PC70BM	Active layer (donor + acceptor)	95
				V ₂ O ₅	HTL	95
				PEDOT:PSS	HTL	96,113,117
				ZnO	ETL	117
				ZnO/PEIE	ETL	95
				AgNWs	Anode	113,121
				P3HT:PCBM	Active layer (donor + acceptor)	88,122,123
				PEDOT:PSS	HTL	122
				ZnO	ETL	122
				CNT	Anode	58
Curtain coating	Yes	0	No	AgNWs	Anode	54,122
Slide coating	Yes	0	No	—	—	—
Multiple slot die coating (Double slot die coating)	Yes	1	No	P3HT:PCBM	Active layer (donor + acceptor)	108
				PEDOT:PSS	HTL	108

scale production and commercialization of cells that are stable, light, low-cost, flexible, as well as simple to manufacture.

Thus, it would be interesting for future research to consider studies of technical-economic-environmental feasibility of each manufacturing technique, as well as the comparative analysis between these techniques. Also due to the fact that OPVs have a strong appeal in the theme of sustainability, research is suggested that consider the analysis of the life cycle of OPVs, according to their manufacturing technique using the circular economy approach.

ACKNOWLEDGEMENT

Our acknowledgment to Mrs Theresa O'Brien de Brito by English language review, and to Mr Irlan Silva for the construction of the figures.

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How to cite this article: Sampaio PGV, González MOA, de Oliveira Ferreira P, et al. Overview of printing and coating techniques in the production of organic photovoltaic cells. *Int J Energy Res*. 2020;44:9912–9931. <https://doi.org/10.1002/er.5664>