

钙钛矿光伏的先进印刷技术研究进展

蒋瑞轩¹, 柯秉灿¹, 朱泽伟¹, 童金辉¹, 卜童乐¹, 黄福志^{1,2}

(1. 武汉理工大学, 材料复合新技术国家重点实验室, 武汉 430070; 2. 先进能源科学与技术广东省实验室佛山分中心佛山仙湖实验室, 广东 佛山 528200)

摘 要: 有机无机杂化钙钛矿太阳能电池具有光电转换效率高、制备成本低等优势, 展现出了巨大的应用潜力。然而, 钙钛矿电池要实现产业化应用, 就必须进行放大, 制备出高效稳定的钙钛矿光伏模组, 而其中高质量钙钛矿吸光薄膜的放大制备尤为关键。印刷是最廉价、绿色的宏量制备技术之一, 也是目前钙钛矿大面积制备所广泛采用的主要技术手段。本文综述了刮涂、狭缝涂布、喷墨打印等 6 种印刷技术的工作原理和特点, 分析了各技术的影响因素和调控机理, 并总结了相应的研究进展, 旨在为未来钙钛矿大面积制备研究和应用提供参考。

关键词: 钙钛矿太阳能电池; 印刷技术; 成核与生长; 大面积光伏模组

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Recent Advances on Printing Technology for Perovskite Photovoltaics

JIANG Ruixuan¹, KE Bingcan¹, ZHU Zewei¹, TONG Jinhui¹, BU Tongle¹, HUANG Fuzhi^{1,2}

(1. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China; 2. Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory, Foshan 528200, Guangdong, China)

Abstract: Perovskite solar cells have a great potential for commercialization due to their advantages of high power conversion efficiency and low cost of manufacturing. However, it is necessary for industrial applications of PSCs to scale up perovskite photovoltaic modules with high efficiency and stability, and the key factor is to scale up high-quality perovskite films. Printing is one of the cheapest and environmental-friendly mass production technologies, and it is also the main technical approach widely used for large-area perovskite fabrication. This review summarized the characteristics and mechanisms of six types of printing methods for the deposition of perovskite films (*i.e.*, blade-coating, slot-die coating, inject-printing, and *etc.*). The influencing factors and controlling strategies were analyzed. This review provided a reference for the future research and application of large-scale perovskite photovoltaics.

Keywords: perovskite solar cells; printing technology; nucleation and growth; large-area photovoltaic modules

太阳能是一种具有无地域限制、无储量限制等诸多优势的清洁可再生能源, 开发和高效利用太阳能资源是解决能源危机、环境污染、实现人类社会绿色可持续发展的重要途径之一。太阳能电池作为

一种可高效利用太阳能资源的清洁能源技术, 一直备受科研界和产业界的青睐。自第一代晶硅太阳能电池和第二代以铜铟镓硒(CIGS)太阳能电池、碲化镉(CdTe)太阳能电池等为代表的薄膜太阳能电池问

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第一作者: 蒋瑞轩(1999—), 男, 博士研究生。

通信作者: 卜童乐(1993—), 男, 博士, 研究员;

黄福志(1976—), 男, 博士, 研究员。

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First author: JIANG Ruixuan (1999—), male, Doctoral candidate.

E-mail: jiangruixuan@whut.edu.cn

Correspondent author: BU Tongle (1993—), male, Ph.D., Professor;

HUANG Fuzhi (1976—), male, Ph.D., Professor.

E-mail: tongle.bu@whut.edu.cn; fuzhi.huang@whut.edu.cn

世以来, 第三代基于纳米技术、绿色环保且高效的新型太阳能电池也已迅速发展起来, 引起了科研界的广泛关注^[1]。尤其是有机/无机杂化钙钛矿太阳能电池(PSCs), 凭借其高的光电转换效率^[2]、低的制备成本^[3]、可制备柔性器件^[4]等优势掀起了近年来光伏领域的研究热潮^[5–7], 其中, 光电能量转换效率(PCE)是评价太阳能电池器件性能的重要指标, 它表征了器件将太阳能转化为电能的能力。根据美国国家可再生能源实验室关于各类太阳能电池效率记录表的报道^[8], 单结固态 PSCs 在 2009 年被第一次报道时 PCE 仅为 3.8%^[9], 仅 13 年后就已达到 26%, 且其叠层器件 PCE 也已达 30%, 可见 PSCs 的研究发展非常迅速, 在产业化方面展现了巨大的发展前景^[10]。然而, 目前大多数实验室对钙钛矿光伏的研究仍停留在旋涂法制备的小面积器件(活性面积小于 1 cm^2)上, 面向产业化大面积器件研究仍处于初始阶段^[10–15]。在钙钛矿走向成熟光伏产业化的道路上, 实现例如卷对卷等快速流水线生产是不可回避的挑战(图 1)^[13–19], 因此进一步大力发展大面积钙钛矿模组非常重要。

钙钛矿光伏器件通常由钙钛矿光吸收层、电子

传输层(ETL)、空穴传输层(HTL)和两端电极构成, 其中钙钛矿光吸收薄膜材料是钙钛矿光伏器件中最关键的组成部分, 因此要实现大面积光伏模组就必须先实现大面积高品质钙钛矿薄膜的制备^[12, 14–15, 20]。旋涂法是实验室科研中最常见的钙钛矿薄膜制备方法^[2, 7, 10], 但是该方法本身存在着原料浪费、薄膜不均匀等问题, 因此并不适用于大面积模组的绿色低碳成本制备。相比之下, 印刷技术^[3, 10, 21]不仅能避免原料浪费, 具有低成本的优势, 而且还能在平米级的尺度上实现规模化的钙钛矿薄膜制备, 这种低成本的可扩大性是连传统晶硅太阳能电池都无法达到的。现有可扩展印刷制备钙钛矿薄膜的策略主要包括刮涂法^[22]、狭缝涂布法^[3]、喷墨打印法^[23]、丝网印刷法^[21]、计量棒涂布法^[24]和喷涂法^[25]等。为了进一步发展这些先进的印刷技术, 理解其制备原理和调控手段尤为重要。对钙钛矿材料, 其结晶过程直接决定了薄膜的形貌和光电子性质, 因此本文首先结合理论模型介绍了钙钛矿晶体形核生长的原理, 然后综述了上述各先进印刷技术的制膜原理、影响因素和改进策略, 最后分析了该领域的研究进展, 为未来大面积钙钛矿光伏的发展提供了科学的参考。

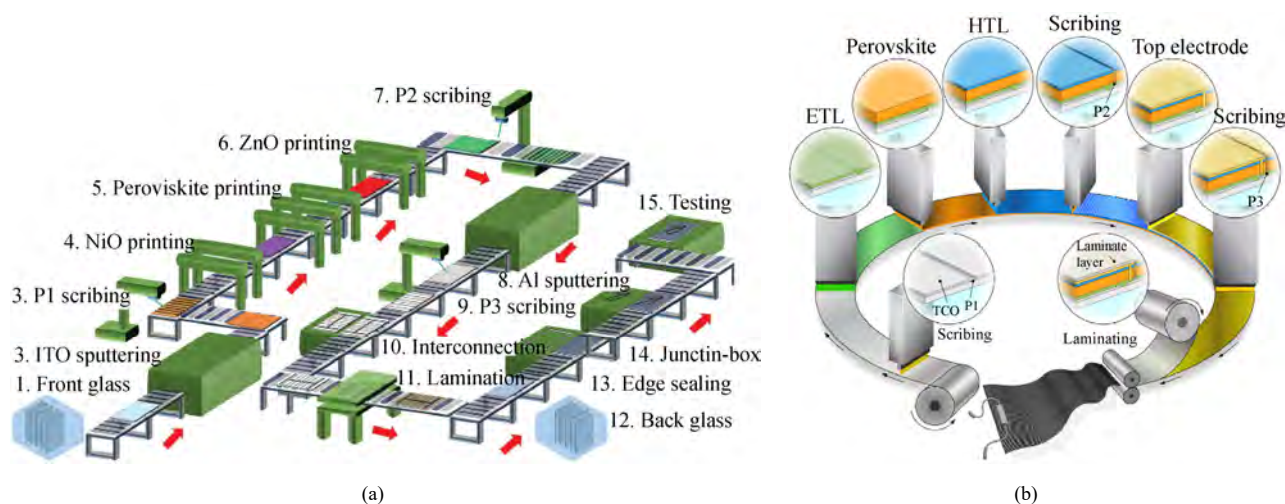


图 1 (a)钙钛矿太阳能模组生产流程示意图^[26]; (b)卷对卷工艺生产钙钛矿太阳能模组示意图^[27]

Fig. 1 (a) Schematic diagram of the manufacturing process of perovskite solar modules^[26]; (b) Schematic illustration of roll-to-roll production of perovskite solar modules^[27]

1 钙钛矿薄膜印刷原理

钙钛矿作为一种离子晶体材料, 其结晶过程直接决定了薄膜的均匀性和致密性, 进而决定了薄膜的光电子性能和器件性能。对于溶液法印刷的钙钛矿薄膜, 其结晶过程中最关键的因素包括形核和生长, 以下分别介绍其原理和调控策略。

在钙钛矿前驱体溶液中, 微粒只有先形成一定尺寸的稳定晶核, 才能进一步生长^[28–29]。对于溶液中的单个微粒来说, 其 Gibbs 自由能表征了其热力学稳定程度, 如式(1)所示。当微粒尺寸极小时, 其自由能随粒径增大而增大。当微粒互相碰撞和结合后, 其聚集体的尺寸就会进一步增大。当聚集体的半径达到临界半径 r^* 时, Gibbs 自由能也同时达到

最大, 即此时微粒的热力学最不稳定。此时, 聚集体就形成了可以进一步增大尺寸的晶核, 可见形核的驱动力正是小分子或前驱体微粒的过剩自由能。当微粒继续增大时, Gibbs 自由能就会随粒径增大而逐渐减小, 即晶核尺寸的继续增大将有利于微粒在热力学上的稳定(图 2a)。

$$\Delta G = \Delta G_s + \Delta G_v = 4\pi r^2 \gamma + (4\pi r^3)/3 \quad (1)$$

其中: G 为总自由能; G_s 为表面自由能; G_v 为体相自由能; r 为微粒半径; γ 为界面能。形核后的生长主要由扩散控制生长和反应控制生长 2 种机理控制^[29]。扩散控制原理如式(2)和式(3)所示, 其中式(2)和式(3)分别展现了扩散通量的微分形式和积分形式。当溶质结合到晶粒表面时, 在晶粒-溶液界面附近的浓度会随之降低, 从而和远处未显著变化的浓度形成浓度差。在浓度差的驱动下, 远处溶质会继续扩散向晶粒表面并结合生长。这就是扩散控制的生长机理。而反应控制生长指的则是反应物在化学势的驱动下直接在晶体表面发生反应并沉积, 从而增大晶粒尺寸的过程, 如式(4)所示。当生长的总速度快于晶粒自身的溶解速度时, 晶体就能产生净生长(图 2b)。

$$dJ = 4\pi r^2 D(dC/dx) \quad (2)$$

$$J = (4\pi r(r+\delta)D)(C_b - C_i)/\delta \quad (3)$$

$$J = 4\pi r^2 k(C_i - C_r) \quad (4)$$

其中: J 为总扩散通量; D 为溶质的扩散系数; δ 为溶质到结晶区域的距离; C_b 为溶液中远离晶粒处的溶质浓度; C_i 为生长浓度; k 为晶粒表面处的化学反应系数; C_r 为半径为 r 的晶粒的溶解度。除生长外, 还会发生小晶粒溶解后沉积在大晶粒上的熟化现象^[28, 30]。这个过程能减少小晶粒并增多大晶粒, 所以非常有利于减少钙钛矿晶界数量及其缺陷。熟化的驱动力同样也是小尺寸晶粒表面过剩的自由能, 影响因素主要包括表面张力和晶体密度等, 如式(5)所示。

$$\ln(C/C_s) = (2\sigma M)/(dRT r_{crit}) \quad (5)$$

其中: σ 为表面张力; M 为晶体摩尔质量; d 为晶体密度; R 为摩尔气体常数; T 为温度; r_{crit} 为临界晶粒半径。钙钛矿晶体的形核与生长都需要消耗溶质, 当形核消耗的溶质更多时, 用于生长的溶质就会相应减少, 最终生成的晶粒数量多而尺寸小; 而当形核消耗的溶质较少时, 用于生长尺寸的溶质相对更多, 则最终生成的晶粒数量少而尺寸大。因此, 形核和生长这 2 个过程是相互制约的。根据 LaMer 成核生长模型可知(图 2c), 当溶质浓度高于最大过

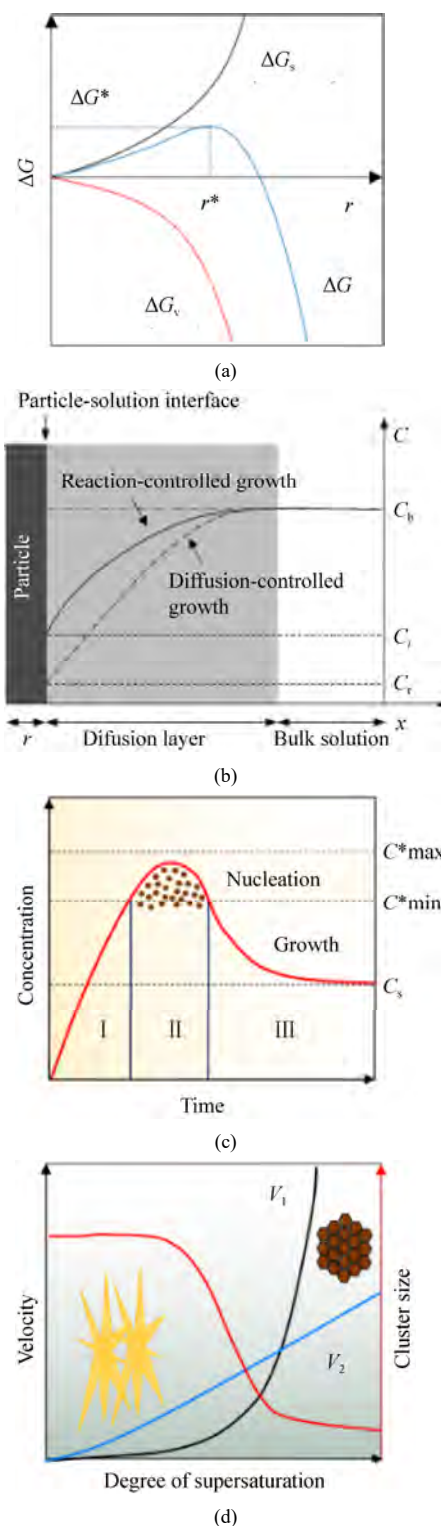


图 2 (a)钙钛矿前驱体溶液中微粒自由能和粒径的关系^[29]; (b)钙钛矿前驱体溶液中晶粒生长的原理示意图^[29]; (c) LaMer 模型示意图^[3]; (d)生长速度和团簇尺寸关于过饱和度的变化趋势^[3]

Fig. 2 (a) Relationship between free energy of particles in perovskite precursor solution and their radii^[29]; (b) Schematic diagram of the crystal growth in precursor solution^[29]; (c) Diagram of the LaMer module^[3]; (d) The variation trend of velocity and cluster size on degree of supersaturation^[3]

饱和浓度时就会发生快速自成核(阶段 II), 之后溶质会因进一步的形核生长而逐渐减少, 并最终达到饱和状态。如果结晶系统快速达到阶段 II, 那么溶质就会更倾向于形核行为而非生长行为, 即生长过程相应受限。在这样快速自成核的条件下, 最终的结晶产物就会是尺寸小而数量多的晶体, 反之则是尺寸大而数量少的晶体。图 2d 为钙钛矿溶液中溶质过饱和程度和晶簇尺寸的关系, 同样说明了快速过饱和是实现薄膜致密化的必要条件。通常情况下, 在 N,N-二甲基甲酰胺(DMF)等常见溶剂中, 钙钛矿自身的生长行为会明显强于形核行为^[31], 这往往会导致薄膜中的晶粒数量少而尺寸大, 晶粒间也就容易产生间隙和孔洞, 随之而来的缺陷就会阻碍载流子传输并降低器件的性能。为了解决这个问题, 目前研究者们从结晶系统的外部 and 内部两个方面提出了一些解决思路。外部辅助方法主要包括吹气辅助法^[31]和反溶剂法^[32], 它们能分别通过蒸发溶剂和提取溶剂的原理使前驱体溶液迅速达到过饱和状态, 促进结晶系统快速达到 LaMer 模型的第 II 阶段, 形成大量小尺寸的晶粒, 抑制晶粒间空隙的产生, 实现薄膜的致密化。结晶系统内部的调控主要指的是墨水成分调控, 如可以采用 2-甲氧基乙醇(2-Me)^[24]等特定溶剂来增快形核过程。

2 钙钛矿薄膜印刷技术的特点和优化策略

2.1 钙钛矿薄膜印刷技术的分类和特性

钙钛矿印刷制备技术(图 3)主要分为刮涂法、狭缝涂布法、喷墨打印法、计量棒涂布法、丝网印刷法以及喷涂法等, 以下分别介绍各方法的技术特性。

刮涂法指的是利用刀片和衬底间的弯月液面来铺展钙钛矿前驱体液膜, 进而结晶形成薄膜的方法(图 3a)^[22]。这种方法工艺简单, 受到了大量研究者的关注和使用。然而, 刮刀下的墨水量是难以控制的, 所以制备出的薄膜往往会存在着不均匀的问题。

狭缝涂布法指的是通过充满溶液的狭缝来铺展液膜, 从而制备钙钛矿晶体薄膜的方法(图 3b)^[33]。因为这种方法可以通过控制系统实现定速供液, 所以能有效解决刮涂法制备薄膜不均匀的问题。狭缝涂布的原理^[33]和接触式 3D 打印类似, 自 2015 年提出以来就成为了制备大面积钙钛矿模组的最重要的方法之一^[34], 同时其给液模式已被报道能够实现柔性器件制备和卷对卷生产^[35–48], 相比刮涂法展现出了更强的产业化潜力。此外, 狭缝涂布除了能实现一步法制备钙钛矿薄膜外, 还能通过两步法的制备策略来提高器件性能的可重复性^[49–50]。

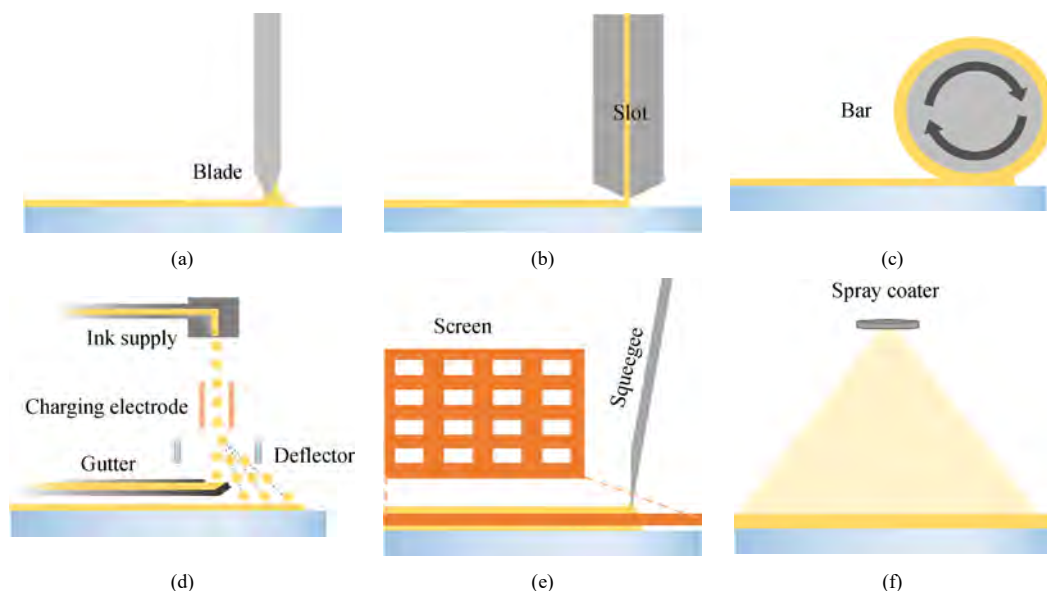


图 3 (a)刮涂法^[22]、(b)狭缝涂布法^[35]、(c)计量棒涂布法^[24]、(d)喷墨示意图法^[51]、(e)丝网印刷法^[21]、(f)喷涂法^[52]的示意图
Fig. 3 Schematic illustration of (a) The blade coating method^[22]. (b) Slot-die coating method^[35]. (c) Bar-coating method^[24]. (d) Inkjet-printing method^[51]. (e) Screen-printing method^[21]. (f) Spray-coating method^[52]

计量棒涂布法指的是通过计量棒或其他棒状物将墨水直接辊压涂布在衬底上, 再形成钙钛矿薄膜

的方法(图 3c), 这种方法虽然尚未解决边缘涂布不均匀的问题, 却仍可直接应用于卷对卷生产的特性

受到了研究者的关注^[24]。

喷墨打印法指的是将钙钛矿溶液直接定量地喷射在衬底上, 然后退火成膜的方法(图 3d), 这种方法可以通过改变墨水浓度或打印层数来实现钙钛矿薄膜厚度的调控, 具有非接触印刷的优势^[51]。然而其墨水只能采用挥发性差且黏度低的, 因此在溶剂选择方面也存在一定限制。

此外, 还有丝网印刷和喷涂法可以用于印刷钙钛矿薄膜。丝网印刷指的是用网格将墨水转移到平面衬底上而成膜的简单技术(图 3e), 操作简单, 但对网格的孔径结构要求较高^[21]。喷涂法是通过超声波等机械振动使墨水以细雾的形式分散在衬底上的方法(图 3f)^[52]。该方法可以产生超细和均匀的雾滴, 非常适合制备均匀液膜, 进而实现钙钛矿薄膜的高均匀性。

从工艺成本的角度来看, 先进印刷技术在生产过程中的墨水浪费均很少, 与浪费约 90% 原材料的旋涂法相比更具经济性^[26]。Song 等对钙钛矿模组的生产进行了系统的成本分析^[26]。在该模型中, 即使组件仅以 16% 的 PCE 运行 30 年, 其平准化度电成本也仅为 4.93~7.90 cents/kW·h, 远远低于传统煤炭供电的价格, 显示出了巨大的产业化潜力和商业化前景。

从生产速度的角度来看, 刮涂、狭缝涂布、计量棒涂布等先进印刷技术还可以结合卷对卷等工艺实现高通量连续生产, 大幅降低了批次生产的成本。相比之下, 喷墨打印的速度非常缓慢, 严重限制了其在大批量生产方面的应用。特别地, 狭缝涂布法兼具成本低、对墨水组成要求低、易实现薄膜均匀性和致密性、可实现卷对卷高通量生产等优势, 因此很可能是实现钙钛矿太阳能电池大面积制备的最佳选择。

2.2 刮涂的影响因素及调控方法

刮涂法指的是在刀片和衬底间形成弯月液面, 进而铺展钙钛矿前驱体液膜并结晶成膜的方法。在刮涂过程中, 最重要的就是要形成合适的弯液面来铺展液膜, 而弯液面则能通过刮刀和衬底的间距、刮涂速度、墨水黏度或添加剂等因素来调控(表 1)。

在工艺方面, He 等从流体力学的角度揭示了弯液面辅助刮涂的原理^[53]。实验表明, 弯液面边缘溶剂的快速蒸发会加速刀片下墨水的对流, 从而补充蒸发损失的墨水, 进而实现刀片下持续的供液(图 4a)。

为了进一步优化结晶动力学, 研究者往往会采

用加热衬底或吹气的辅助策略来促进钙钛矿晶体的快速自成核。如 Deng 等发现在过低温度的衬底上刮涂时, 薄膜会因为缓慢干燥而出现不致密的问题^[77]。类似地, Zhong 等则注意到在较低温度(25~80 °C)的衬底上刮涂时, 易产生碘化铅(PbI₂)的中间相而导致薄膜不均匀; 而在升温后(100~150 °C)的衬底上刮涂时, 则未发现上述不利的中间相^[78]。因此, 适当提高衬底温度也有利于提高钙钛矿薄膜的致密性。

在墨水方面, 主要可以通过引入添加剂来改善钙钛矿薄膜的性质。甲胺盐酸盐(MACI)是一种广泛使用的添加剂, 它容易和前驱体形成易转化为 α -相钙钛矿的中间相, 同时能起增大晶粒的作用^[79]。二甲亚砜(DMSO)也能和钙钛矿前驱体配位形成稳定的中间相, 因此也常常被应用于墨水添加剂^[80]。然而, 由于 DMSO 沸点较高(189 °C)且其钙钛矿前驱体中间相过于稳定, 较难在退火过程中有效除去, 因此研究者们也期望选取配位较弱或沸点较低的其他添加剂来取代 DMSO^[81]。如 Bi 等发现了低配位的 γ -丁内酯(GBL)可以提高 PbI₂ 在墨水中的溶解度, 并能调节溶剂的蒸发速率^[82]。Deng 等则使用了可挥发且非配位的乙腈(ACN)与 2-Me 来刮涂钙钛矿薄膜(图 4b~图 4d)^[64]。在室温条件下, 可观察到非挥发性的 ACN 是缓慢逸出的, 这有助于增大钙钛矿的晶粒并优化层间接触。最终, 开孔面积为 63.7 cm² 的模组展现了 16.4% 的认证效率。特别地, Chen 等^[60]发现钙钛矿会在液膜/空气的界面开始结晶, 这些优先形成的固相外壳也会阻碍 DMSO 分子逸出, 为了克服这个问题, 采用固态碳酰肼(CBH)替代部分 DMSO。CBH 不仅可以和 Pb²⁺ 形成强配位作用, 还可以减少退火时钙钛矿薄膜中因 DMSO 逸出而形成的孔洞(图 4e)。此外, CBH 自身的还原性还可以抑制 Γ 在光照时氧化为 I₂, 活性面积分别 18.1 cm² 和 50 cm² 的 p-i-n 型模组分别展现了 19.3% 和 19.2% 的认证效率。

Bu 等探明了 N-甲基吡咯烷酮(NMP)添加剂对刮涂钙钛矿薄膜结晶的影响机理^[22]。实验表明, NMP 可以优先与 PbI₂ 络合, 因此在干燥过程中能直接以 PbI₂·NMP 络合物的形式成核结晶, 大大改善了薄膜的致密性; 然后再在退火过程中与嵌入在结构中的甲脒氢碘酸盐(FAI)和碘化铯(CsI)进行原位反应而直接形成具有光伏效应的 α -相钙钛矿, 大大提高了薄膜晶体质量, 印刷制备的 5 cm × 5 cm 微型组件效率突破 20%。随后, 进一步在钙钛矿前

驱体墨水中引入了 MACl, 发现 MACl 可以显著的降低钙钛矿的形成能, 实现 Ostwald 熟化, 优化钙钛矿的晶体生长质量(图 4f), 实现致密大晶粒钙钛矿薄膜的制备。研究者基于这种原理对墨水 and 工艺进行了优化, 从而成功使开孔面积高达

205 cm² 的模组展现出了 15.3% 的效率, 并表现出了优异的运行稳定性。类似地, Yang 等^[83]在刮涂过程中也引入了 NMP 以形成稳定的 FAI·PbI₂·NMP 中间相, 并通过优化的退火工艺将其直接转换为纯 α -FAPbI₃。

表 1 刮涂法制备活性面积不小于 1 cm² 器件的处理方法和参数表

Table 1 Processing methods and parameters of devices with active area not less than 1 cm² prepared by blade-coating method

Device structure	Power conversion efficiency/% (R/F)	Area/cm ²	Area type	Certified	Process	Reference
FTO/SnO ₂ /FA _{0.88} CS _{0.12} PbI ₃ /Spiro-OMeTAD/Au	15.3*	205	Aperture	Yes	Add MACl and NMP	[22]
FTO/SnO ₂ QDs/ZnO-S/FA _{0.9} CS _{0.1} PbI ₃ /Spiro-OMeTAD/Au	18.73/21.39	36	Total	No	Use FTO/SnO ₂ QDs/ ZnO-S structure	[54]
ITO/PTAA/CS _{0.05} FA _{0.95} PbI ₃ /PFBS-C ₁₂ /Ag	18.9*	53.6	Active	No	Optimize ETL	[55]
FTO /c-TiO ₂ /mp-TiO ₂ / MAPbI ₃ /CB/Ag	19.68 (average)	100	Total	No	Optimize ETL	[56]
FTO/SnO ₂ /FA _{0.83} CS _{0.17} Pb(I _{0.9} Br _{0.1}) ₃ /Spiro-OMeTAD/Au	18.4/18.8	10	Active	Yes	Add ammonium acetate (NH ₄ Ac)	[57]
ITO/PTAA/CS _{0.05} FA _{0.95} PbI ₃ /PCBM/Ag	9.96*	1	Active	No	Use Alkyl xanthate to disperse nickel oxide (NiO _x)	[58]
FTO/SnO ₂ /MAPbI ₃ /Spiro-OMeTAD/Au	—/15.65	10.08	Active	No	Add arginine acid (Arg)	[59]
ITO/PTAA/MA _{0.6} FA _{0.4} PbI ₃ /C ₆₀ /BCP/Cu	19.3*	18.1	Aperture	Yes	Add CBH	[60]
ITO/PTAA/MA _{0.6} FA _{0.4} PbI ₃ /C ₆₀ /BCP/Cu	19.2*	50	Aperture	Yes	Add CBH	[60]
FTO/SnO ₂ /CS _{0.15} FA _{0.85} PbI _{2.55} Br _{0.45} /Spiro-OMeTAD/Au	17.71*	10	Active	No	Add DMPU	[61]
ITO/SnO ₂ /MA _{0.9} GA _{0.1} PbI ₃ /P3HT/Ta-WO _x /C	15.3*	25	Total	No	Add GACl	[62]
ITO/PETDOT:PSS/PTAA/MAPbI ₃ /PC ₆₁ BM/BCP/Cu	16.48/16.61	1	Aperture	No	Add thiourea	[63]
ITO/PTAA/MAPbI ₃ /BCP/ Ag	16.9*	63.7	Active	Yes	Add CAN and 2-Me	[64]
ITO/PTAA/ MAPbI ₃ /PC ₆₁ BM/BCP/Ag	15.38*	10.08	Active	No	Add S-benzyl-L-cysteine (SBLC)	[65]
FTO/SnO ₂ /(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Spiro-OMeTAD/Au	16.54/13.17	100	Total	No	Add tributyl phosphate (TBP)	[66]
FTO/ZnS-ZnO/Crown-modified FACsPbI ₃ /Spiro-OMeTAD/Au	16.05/16.69	8.00	Active	No	Add crown ether	[67]
FTO/ZnS-ZnO/Crown-modified FACsPbI ₃ /Spiro-OMeTAD/Au	12.64/13.84	49.0	Active	No	Add crown ether	[67]
ITO/PTAA/MAPbI ₃ /C ₆₀ /BCP/Cu	15.45/15.86	42.9	Active	No	Add NH ₄ Ac	[68]
ITO/NiO _x /MAPbI ₃ /PCBM/BCP/Ag	16.66/16.71	1	Active	No	Vacuum quenching	[69]
Flexible PET/ITO/PEDOT: EVA/MA _{0.7} FA _{0.3} PbI ₃ /PC ₆₁ BM/Ag	16.34/17.61	31.20	Active	No	Use (PEDOT:EVA) as HTL	[70]
ITO/PTAA/BHC-modified MAPbI ₃ /C ₆₀ /BCP/Cu	18.20*	35.8	Active	No	Add benzene hexachloride (BHC)	[71]
Flexible PEN/ITO/PTAA/GBA-modified FA _{0.7} MA _{0.25} CS _{0.05} Pb(I _{0.93} Br _{0.07}) ₃ /PCBM/BCP/Ag	13.26/14.48	10.64	Active	No	Add 4-guanidine butyric acid (GBA)	[72]
ITO/PTAA/MAPbI ₃ /PCBM/BCP/Cu	—/18.26	1.96	Total	No	Add Porphyromononium (ZnP)	[73]
FTO/c-ZnO-ZnS/m-TiO ₂ /MAPbI ₃ /Spiro-OMeTAD/Au	—/15.79	16	Total	No	Add Tetrabutylammonium bromide (TBAB)	[74]
FTO/TiO ₂ /MA _{0.7} FA _{0.3} PbI ₃ /Spiro-OMeTAD/Au	11.6/16.3	10.36	Active	No	Add NMP and pre-heat the substrate	[75]
ITO/PTAA/MAPbI ₃ /C ₆₀ /BCP/Cu	14.2/15.0	33	Aperture	Yes	Add L- α -phosphatidylcholine	[53]
ITO/PTAA/MAPbI ₃ /C ₆₀ /BCP/Cu	14.7/14.9	57.2	Active	Yes	Add L- α -phosphatidylcholine	[53]
ITO/PTAA/FA _{0.85} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃ /PCBM/C ₆₀ /BCP/Cu	18.3*	1	Total	No	Add sulfonic zwitterions	[76]

* after PCE indicates that only the highest efficiency is provided without indicating forward or reverse scanning.

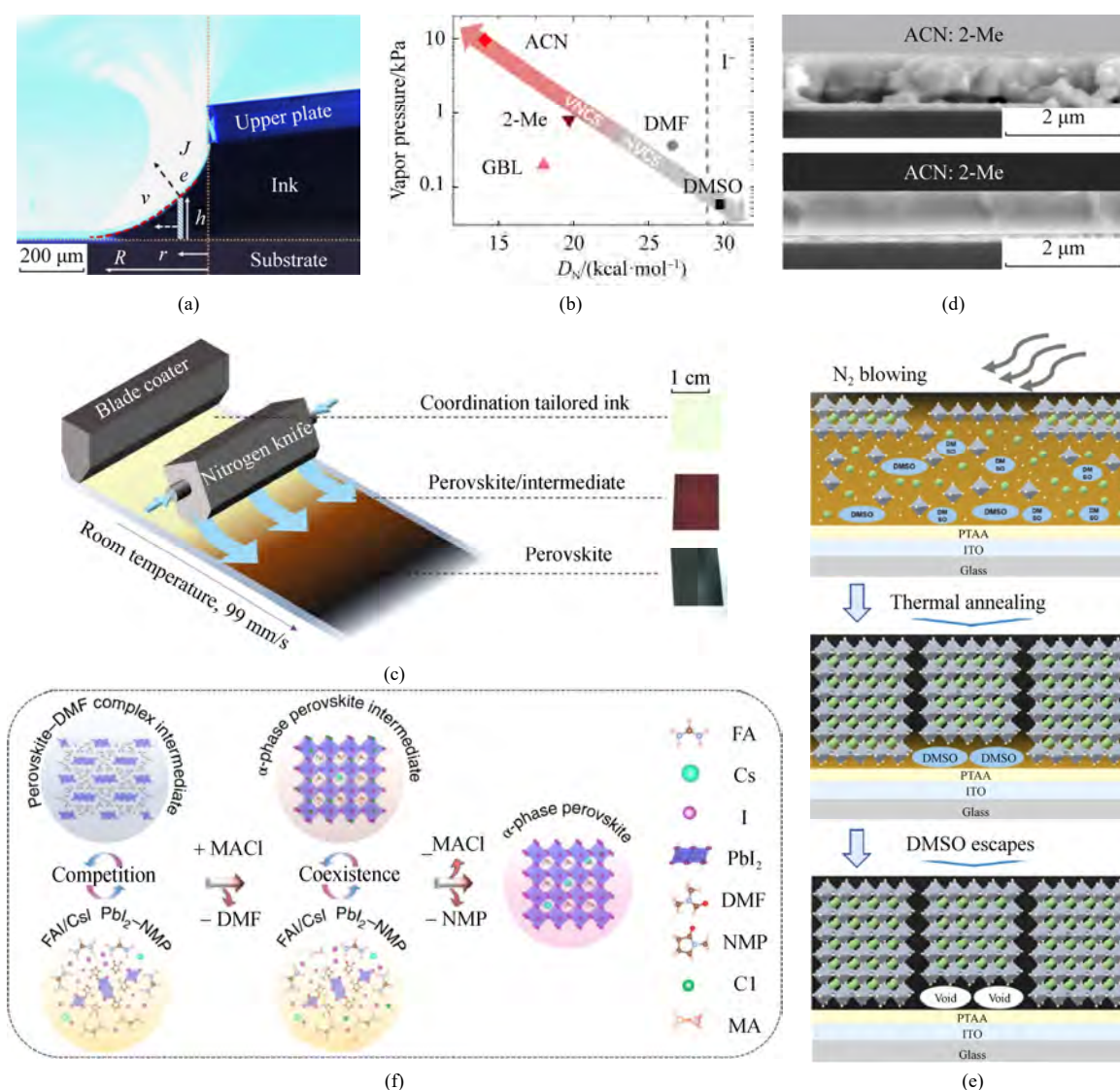


图 4 (a)墨水弯月面与刮刀间的光学显微照片^[53]; (b)溶剂蒸气压和碘离子及溶剂电子给体数(D_N)间的关系^[64]; (c)在室温下以 99 mm/s 的速度对钙钛矿膜进行 N₂吹气处理的示意图^[64]; (d)不同混合溶剂制备的钙钛矿薄膜截面的扫描电子显微镜照片^[64]; (e)钙钛矿界面形成孔洞过程的示意图^[60]; (f)向使用 DMF/NMP 混合溶剂的钙钛矿前驱体溶液中添加 MACl 后钙钛矿结晶的步骤示意图^[22]

Fig. 4 (a) Optical micrograph of the cross-view meniscus ink between a lower flat, movable substrate and an upper stationary plate^[53]; (b) Relationship of vapor pressure and donor number (D_N) of solvents and iodide ion^[64]; (c) Schematic illustration for N₂-knife-assisted treatment of perovskite film using a speed of 99 mm/s at room temperature^[64]; (d) Cross-section scanning electron microscope images of perovskite films prepared with different solvent mixtures^[64]; (e) Schematic diagram of how the voids are formed at the perovskite-substrate interfaces^[60]; (f) Schematic of the crystallization steps with addition of MACl to the DMF/NMP solvent based perovskite precursor solution^[22]

2.3 狭缝涂布的影响因素及调控方法

狭缝涂布法指的是利用狭缝在衬底上铺展墨水进而结晶成膜的方法(表 2)。和刮涂相比,狭缝涂布使用的墨水是通过控制系统均匀补充的,所以其涂布过程还受供墨流体力学的影响。Whitaker 等探究了供墨速度和涂布头移动速度间的关系(图 5a)^[84]。当供墨缓慢时,墨水不足以覆盖衬底,所以薄膜也就无法完全覆盖;而供墨过快时,溶液的弯月面就会受力膨胀,沉积厚度随之增大,钙钛矿薄膜会从

约 680 nm 的正常厚度增加到 1 μ m 以上。Burkitt 等更深入地探究了影响狭缝涂布弯月面的因素。认为对于狭缝涂布的低流量墨水,控制墨水的最低流量极限和弯月面破裂极限是实现均匀液膜的关键因素^[85]。对于弯液面[见式(6)]。当墨水流速 v 低于最低流量极限时,过低的 Ca 就会使得液体铺展过程不稳定,从而使薄膜出现不均匀的问题。此外,当狭缝和衬底的间距 H 减小时,液膜的厚度 t 会增大, Ca 也对应越大,液膜的铺展过程也就更稳定[见式(7)]。

$$Ca = \frac{\mu v}{\sigma} \quad (6)$$

其中： μ 为毛细管数 Ca 和墨水的黏度； v 为流体线速度； σ 为表面张力。

$$Ca_{\text{lowflow}} = \frac{\mu V_{\text{max}}}{\sigma} = 0.65 \left(\frac{2}{\frac{H}{t} - 1} \right)^{\frac{3}{2}} \quad (7)$$

表 2 狭缝涂布法制备活性面积不小于 1 cm^2 器件的处理方法和参数表

Table 2 Processing methods and parameters of devices with active area not less than 1 cm^2 prepared by slot-die method

Device structure	Power conversion efficiency/% (R/F)	Area/ cm^2	Area type	Certified	Process	Reference
ITO/SnO ₂ /MAPbI ₃ /Spiro-OMeTAD/MoO _x /Ag	11.24/–	1	Active	No	Use intense pulse light annealing	[47]
ITO/NiO NPs/Cs _{0.17} FA _{0.83} Pb(I _{0.87} Br _{0.13}) ₃ /PCBM/ZnO NPs/Ag	16.06/13.50	1	Active	No	Heat the slot-die coater	[86]
FTO/NiO/MAPbI ₃ /PCBM/BCP/Ag	17.7/–	1	Total	No	Add GBL and DMSO	[87]
FTO/TiO ₂ /ZrO ₂ /MAPbI ₃ /C	–/11.1	1.5	Active	No	Multilayer slot-die coating	[88]
ITO/SnO ₂ /MAPbI ₃ /Spiro-OMeTAD/Ag	15.1*	2.1	Active	No	Multilayer slot-die coating and vacuum quenching	[89]
PET/ITO/SnO ₂ /FAPbI ₃ /Spiro-OMeTAD/Au	10.68/8.20	5	Total	No	Coating using a sheet of paper	[90]
FTO/TiO ₂ /FAPbI ₃ /PC ₆₁ BM/Ag	19.0/19.6	7.92	Active	No	Stabilize the phase during coating	[91]
ITO/poly(3,4-ethylenedioxythiophene):poly(ITO)/PEDOT:PSS/MAPbI ₃ /C ₆₀ /PCBM/BCP/Ag	8.3*	10	Active	No	Add PbAc ₂ and PbCl ₂	[92]
FTO/c-TiO ₂ /SnO ₂ /FA _{0.55} Pb(I _{0.96} Br _{0.04}) ₃ /Spiro-OMeTAD/Au	15.2/17.5	12	Aperture	No	Add DMSO	[50]
ITO/2PACz/MAPbI ₃ /C ₆₀ /Cu	3.79/3.87	12.56	Active	No	Add DMSO	[93]
PET/ITO/SnO ₂ /Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ /Spiro-OMeTAD/Au	15.10/15.22	16.07	Active	No	Prepare SnO ₂ by slot-die coating	[94]
FTO/SnO ₂ /FA _{0.83} Cs _{0.17} PbI ₃ /2D-KPF ₆ /Spiro-OMeTAD/Au	18.9/19.3	17.1	Active	Yes	Add NMP	[3]
FTO/SnO ₂ /FA _{0.83} Cs _{0.17} PbI ₃ /2D-KPF ₆ /Spiro-OMeTAD/Au	19.22/19.54	65.0	Active	No	Add NMP	[3]
FTO/SnO ₂ /Cs _{0.05} MA _{0.4} FA _{0.55} Pb(I _{0.96} Br _{0.04}) ₃ /Spiro-OMeTAD/Au	–/17	18.1	Active	No	Add DMSO	[95]
ITO/NiO _x with LS1/ MAPbI ₃ /PCBM/BCP/Ag	14.9 (Average)	19.16	Aperture	No	Add self-assembled donor–acceptor dyad molecules	[96]
FTO/NiMgLiO/FA _{0.83} Cs _{0.17} PbI _{2.83} Br _{0.17} /LiF/C ₆₀ /BCP/Bi/Ag	16.63 (Quasi-stabilized efficiency)	20.77	Active	Yes	Add DPSP	[97]
FTO/TiO ₂ /FAPbI ₃ /Spiro-OMeTAD/Au	16.89/17.86	26.4	Active	No	Vacuum quenching	[98]
ITO/PTAA/FAPbI ₃ /C ₆₀ /SnO ₂ /Ag	17.26/17.56	57	Active	No	FAI post-treatment	[99]
FTO/SnO ₂ /FAPbI ₃ /Spiro-OMeTAD/Au	15.63/16.22	57.5	Active	No	Add CsPbBr ₃ and KPb ₂ Br ₅	[100]
FTO/TiO ₂ /ZrO ₂ /MAPbI ₃ /Carbon	–/12.87	60.08	Active	No	Use TiO ₂ /ZrO ₂ /Carbon structure	[101]
FTO/SnO ₂ NPs/MAPbI ₃ /Spiro-OMeTAD/Au	17.3 (Average)	100	Total	No	Add DMSO	[49]
PET/ITO/PEDOT: PSS/MAPbI ₃ /PCBM/BCP/Ag	12.2*	100	Total	No	Multilayer slot-die coating	[42]
ITO/c-TiO ₂ /M	11.8*	142	Active	No	Laser processing	[102]
APbI ₃ –xCl/Spiro-OMeTAD/Au	18.6/18.6	174	Active	No	Slot-die coating perovskite and vacuum deposit the NiO _x	[103]
FTO/SnO ₂ /Cs _{0.1} FA _{0.9} PbI ₃ /PCBM/Ag	11.2*	300	Active	No	Add phenylalanine (Phe)	[104]

Note: * after PCE indicates that only the highest efficiency is provided without indicating forward or reverse scanning.

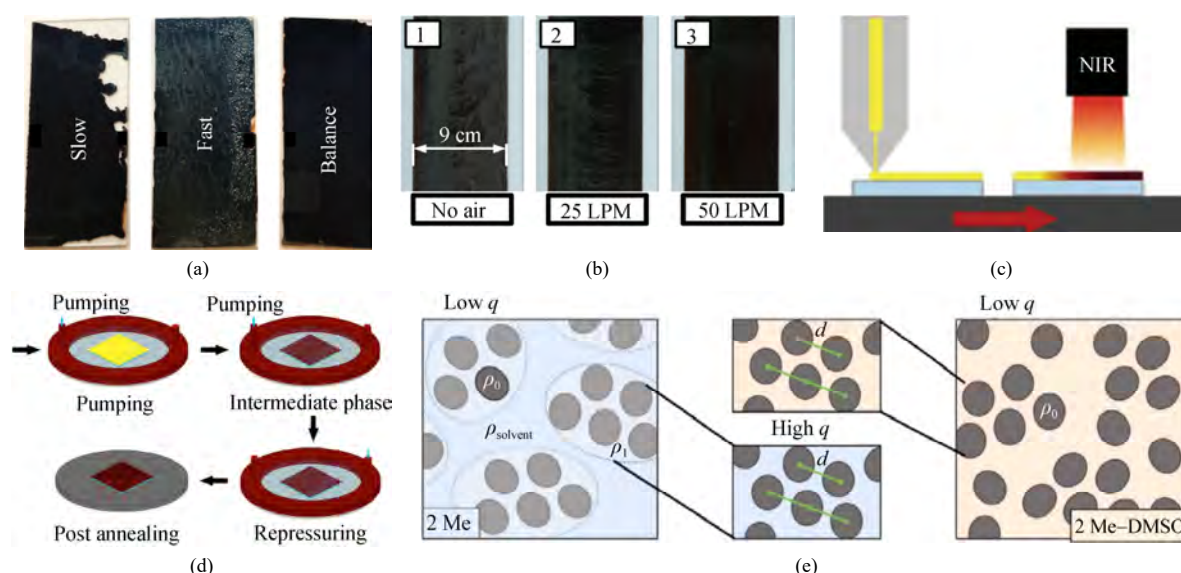


图 5 (a) 钙钛矿薄膜致密性和均匀性与狭缝涂布速率的关系^[84]; (b) 钙钛矿薄膜致密性和均匀性与气流速率的关系^[85]; (c) 近红外光退火工艺示意图^[105]; (d) 真空淬火工艺示意图^[89]; (e) 添加剂影响胶粒形成的示意图^[93]

Fig. 5 (a) Relationship between the film compactness and uniformity and the coating speed^[84]; (b) Relationship between the film compactness and uniformity and the air flow speed^[85]; (c) Schematic diagram of NIR assisted annealing strategy^[105]; (d) Schematic of the vacuum quenching strategy^[89]; (e) Schematic diagram of the additive effect on adjusting colloidal particle formation^[93]

吹气工艺也能显著影响钙钛矿薄膜的形成过程。实验表明^[85], 无任何外界辅助的薄膜形貌不均匀且存在大量孔洞; 经过 25 LPM 气量处理的薄膜虽已比较均匀, 但仍存在一些孔洞; 而经过 50 LPM 气量处理的薄膜则显示了优越的均匀性和致密性(图 5b)。除吹气法之外, 热处理也是调控晶体生长学的重要方法。Kim^[41]等在室内湿度的条件下, 在 130 °C 的衬底上通过卷对卷狭缝涂布法制备了钙钛矿薄膜, 改善了薄膜的形貌和器件性能。同样在空气条件下, Vijayan 等^[106]在 90 °C 衬底上制备了粒径高达 100~200 μm 的钙钛矿薄膜。Cotella 等^[107]则发现在有吹气法辅助的基础上, 若采用 65 °C 预热的衬底, 则能实现形貌更致密的钙钛矿薄膜。类似地, 大量研究都将吹气法和衬底预热法结合起来, 这样从两个角度就能更容易地调控钙钛矿的结晶动力学^[3, 46, 107-109]。在加热方面, 除传统的热传导加热外, 一些研究还采用了近红外(NIR)或其他高强度光来实现加热。如 Huang 等就采用了 NIR 辅助退火技术, 先后通过“逐页打印”^[110]和全狭缝涂布工艺^[105]制备了钙钛矿光伏器件, 这种退火方式能显著提高钙钛矿薄膜的制备速度和结晶质量(图 5c)。此外, Ham 等还提出了反溶剂和吹气协同作用的干燥策略, 可以实现卷对卷的大面积快速生产^[45]。此外, 涂布时的气压同样也能有效控制结晶的热动力学(图 5d)。Du 等发现高压氮气的氛围可以提高钙钛

矿中间相的稳定性, 进而扩大狭缝涂布的操作窗口^[91]。和高压相反的是, 真空淬火也是一种处理狭缝涂布钙钛矿湿膜的工艺^[89, 98], Gu 等采用这种技术制备了其活性面积为 26.4 cm^2 的模组, 其 PCE 达到了 17.86%^[98]。

除了工艺调控外, 墨水添加剂本身在很大程度上也影响着狭缝涂布薄膜和器件的性能。目前应用于狭缝涂布的添加剂包括醋酸铅 (PbAc_2)^[36, 92, 111]、环己基-2-吡咯烷酮 (CHP)^[107]、DMSO^[39, 87, 93, 107]、 γ -丁内酯(GBL)^[87]、2-丁氧基乙醇(2-BE)^[39]、氯化铅 (PbCl_2)^[92]、氯化铵(NH_4Cl)^[40]、2-噻吩乙基氯化铵 (TEACI)^[112]、N-甲基吡咯烷酮(NMP)^[3]、透明质酸溴(HABr)^[113]、二苯基亚砷(DPSO)^[97]、醋酸甲胺 (MAAc)^[114]、甲脒氯(FACI)^[89]、MACI^[89]、3-烯丙基氧基-1,2-丙二醇(AP)^[115]、丙烯酸羟乙酯(HEA)^[116]、二甘醇酸 (DA)^[117]、聚(3,4-亚乙二氧基噻吩)-聚(苯乙烯磺酸)^[48]、碘化胍(GAI)^[48]、三溴合铅酸铯 (CsPbBr_3)^[100]、五溴合铅酸钾(KPb_2Br_3)^[100]、苯丙氨酸 (Phe)^[104]、甲胺铅碘盐(MAPbCl_3)^[118]等。添加剂的作用主要有调控钙钛矿结晶和钝化缺陷 2 个方面。其钝化效果主要是凭借材料带电性的官能团或离子实现的, 如 TEACI^[112]、AP^[115]等路易斯酸、碱就能有效钝化钙钛矿中的带电缺陷, 促进载流子传输并提高器件的电压和电流。然而, 研究者们更关注于如何通过添加剂调节相转变, 同时使狭缝涂布

法制备的薄膜更致密、更均匀。如 Kamaraki 等^[111]发现醋酸铅可以加速狭缝涂布过程中钙钛矿的结晶,而 Lee 等则利用了醋酸铅和氯化铅协同的效果,加快了钙钛矿的结晶速度,实现了致密的形貌^[92]。DMSO 作为一种常见的液态添加剂,在狭缝涂布中也起着生成稳定中间相和促进结晶的作用^[39, 87, 93, 107]。和刮涂的相关报道类似,研究者们也同样试图寻找一些其他添加剂来替代 DMSO,进而优化钙钛矿的结晶过程和薄膜形貌。如 Li 等^[93]通过小角 X 射线散射(SAXS)测试对比了 2-Me 基墨水有无 DMSO 添加剂的区别,结果表明纯 2-Me 基墨水在低 q 值时会聚集形成多孔大尺寸的 MAPbI₃-2-Me 中间相胶

粒,而添加 DMSO 后则有利于均匀分散中间相胶体(图 5e),进而抑制多孔中间相的形成并使薄膜致密化。Yang 等则使用了 DPSO^[97]来取代 DMSO。DPSO 和碘化铅可以发生强络合反应,这样就能最大限度地减小溶剂或添加剂与钙钛矿前驱体溶质间的相互作用能,进而改善形核动力学,提高钙钛矿的稳定性,器件在 10 000 h 的光照/黑暗条件下仍保留了 97%的初始 PCE。

2.4 计量棒涂布的影响因素及调控方法

计量棒涂布法被认为是能直接应用于卷对卷生产的制备方法,主要影响因素包括涂布转速、衬底温度、墨水黏度、墨水浓度和涂布间隙等(表 3)。

表 3 计量棒涂布法制备活性面积不小于 1 cm² 器件的处理方法和参数表

Table 3 Processing methods and parameters of devices with active area not less than 1 cm² prepared by bar-coating method

Device structure	Power conversion efficiency/% (R/F)	Area/cm ²	Area type	Certified	Process	Reference
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ (MAPbI ₃)/PCBM/Ag	12.87/13.03	2.1	Active	No	Use anti-solvent of IPA	[119]
FTO/SnO ₂ / MAPbI ₃ /Spiro-MeOTAD/Au	17.82*	100	Totoal	No	Using perovskite cluster-containing solution	[120]
FTO/TiO ₂ /MAPbI ₃ /Spiro-MeOTAD/Au	12.82/14.95	1	Active	No	Add CHP	[121]
FTO/SnO ₂ /(FAPbI ₃) _{0.875} (CsPbBr ₃) _{0.125} /Spiro-MeOTAD/Au	16.01/17.01	25	Totoal	No	Add HMPA	[122]
FTO/TiO ₂ /(FAPbI ₃) _{0.95} (MAPbBr ₃) _{0.05} /Spiro-MeOTAD/Au	17.53*	31	Aperture	Yes	Air assisted coating and add CHP	[24]

* after PCE indicates that only the highest efficiency is provided without indicating forward or reverse scanning.

Jeong 等采用甲胺(MA)气体介导的方法制备了用于计量棒涂布的钙钛矿墨水。研究者们首先将 MAPbI₃ 晶体和含有 MA 液体的烧杯一起放在封闭的容器中,随着 MA 在室温下逐渐蒸发,他们发现暴露于 MA 蒸汽的 MAPbI₃ 晶体会转变为黄色的黏性液体。当直接将该液体作为墨水进行计量棒涂布时,只要选取速度慢、棒与衬底间隙小的涂布条件,就能制备出致密的钙钛矿薄膜(图 6a)^[120]。由于 MA 气体的蒸发速率比成膜速度快,所以在过慢的成膜速度下(小于 5 mm/s)实现稳定成膜是不可能的。为了解决其他高黏性墨水干燥过慢的问题,研究者还尝试通过适当升高衬底温度来缩短干燥时间。Liu 等^[119]指出,在较低的温度下薄膜干燥时间过长,严重延缓了晶体生长的过程,溶液使薄膜出现孔洞;而升温的衬底能有效促进钙钛矿液膜的干燥,但过快的干燥速度也可能导致薄膜表面粗糙等问题。反溶剂处理也能调控钙钛矿薄膜的均匀性和晶粒尺寸,如可以采用异丙醇(IPA)来加速钙钛矿的形核过程,进而优化薄膜的致密度^[119]。在钙钛矿前驱体溶液中加入添加剂也能调控钙钛矿结晶过程和薄膜形貌。如 Ju 等通过引入 CHP 形成了致密且光滑的大面积 MAPbI₃ 中间相薄膜,进而使之转变为形貌致

密的钙钛矿薄膜(图 6b)。该项工作制备的活性面积为 1 cm² 的器件 PCE 达到了 14.95%^[121]。

2.5 喷墨打印的影响因素及调控方法

喷墨打印指的是先利用充电电极使墨水液滴带电,然后再由导流板诱导带电液滴形变并喷射在衬底上而结晶成膜的方法。对于喷墨打印,决定薄膜形貌和性能的关键因素包括衬底热处理工艺和墨水成分(表 4)。

喷墨打印的基本流程如图 7a 所示^[51],其中衬底热处理是十分关键的环节。Li 等^[126]研究了衬底温度对钙钛矿晶体形貌的影响,发现衬底达 50 °C 时制备的薄膜最致密,器件效率也最高(12.3%)。真空退火也能改善钙钛矿的结晶和形貌。Mathies 等^[127]发现未做退火处理的钙钛矿表面非常粗糙和不致密,而真空退火 2 min 和 5 min 后的薄膜表面就能变得致密和平整。Mathies 等^[128]通过调整喷墨打印的液滴间距,在 175~780 nm 的宽范围内控制了钙钛矿层厚度,调节了晶粒尺寸,优化了器件性能(图 7b)。除了常见的一步法喷墨打印策略外, Li 等^[23]还使用喷墨打印技术实现了两步法制备钙钛矿薄膜,而且还通过打印液滴的等距排列策略阻绝了溶质间的自由扩散或对流,有效提高了薄膜的均匀性,其小型 PSCs 的 PCE 可达 18.64%。

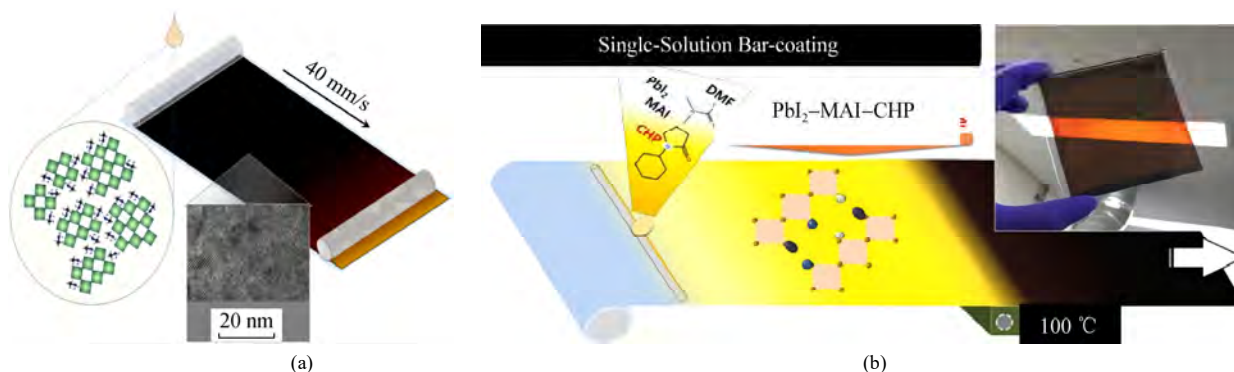


图 6 (a)高通量的计量棒涂布法制备钙钛矿薄膜示意图^[120]; (b)中间相调控的计量棒涂布法制备钙钛矿薄膜示意图^[121]
Fig. 6 (a) Schematic illustration of high-speed bar-coating method for preparing perovskite film^[120]; (b) Schematic illustration of intermediate phase controlled bar-coating method for preparing perovskite film^[121]

表 4 喷墨打印法制备活性面积不小于 1 cm² 器件的处理方法和参数表

Table 4 Processing methods and parameters of devices with active area not less than 1 cm² prepared by inject-printing method

Device structure	Power conversion efficiency/% (R/F)	Area/cm ²	Area type	Certified	Process	Reference
FTO/c-TiO ₂ /m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /CH ₃ NH ₃ PbI ₃ /Spiro-OMeTAD/Au	17.74*	2.02	Active	No	Precisely micro-droplets control	[23]
ITO/NiO _x /Cs _{0.1} MA _{0.15} FA _{0.75} Pb(I _{0.85} Br _{0.15}) ₃ /C ₆₀ /BCP/Au	18.1/21.6	10.5	Active	No	Inject-printing thick perovskite film	[51]
PEN/Ag NWs/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /PC ₇₁ BM/PEI/Ag NWs	16.78*	120	Active	No	Annealing in EA vapor	[123]
ITO/NiO _x /Cs _{0.10} FA _{0.75} MA _{0.15} Pb(Br _{0.15} I _{0.85}) ₃ /PCBM/BCP/Au	16.5/17.2	1.21	Active	No	Multilayer inject-printing	[124]
ITO/Spiro-TTB/MAFPbI ₃ /C ₆₀ /BCP/Au	13.7/14.1	4	Active	No	Inject-printing thick perovskite film	[51]
ITO/PTAA/4F-PEA ₂ MA ₄ Pb ₅ I ₁₆ /C ₆₀ /BCP/Ag	12.87/13.03	1	Active	No	Add 4-FPEA	[125]

Note: * after PCE indicates that only the highest efficiency is provided without indicating forward or reverse scanning.

在墨水成分方面, 为避免因溶剂蒸发而导致喷嘴堵塞, 喷墨打印应选择不易挥发的高沸点溶剂来配制墨水。如 Li 等^[126]和 Mathies 等^[127]分别使用了高沸点的正丁内酯和 γ -丁内酯作为墨水的高沸点溶剂。除沸点外, 墨水的黏度、表面张力和密度也是影响打印效果的重要因素。使用添加剂也能有效控制钙钛矿的成核和生长, 从而得到结晶度高且均匀的钙钛矿薄膜。Gheno 等^[129]发现在钙钛矿墨水中加入氯化物或溴化物有利于增加墨水的润湿性(图 7c), 从而提高墨水在多孔 ETL 材料中的浸润程度。Huckaba 等^[130]在墨水中添加了 2% 的双(乙酰丙酮基)二异丙基钛酸酯溶液(TAA, 75%异丙醇)来优化界面接触, 器件的 PCE 可从 12.56% 增加到 16.1%。Barbara 等^[125]使用了 4-氟苯甲基铵(4-FPEA)作为间隙阳离子来控制钙钛矿的结晶过程, 从而提高薄膜的结晶度和均匀性。

2.6 其他印刷方法的影响因素和调控方法

除了刮涂、狭缝涂布、计量棒涂布和喷墨打印外, 还有丝网印刷和喷涂等印刷方法, 以下分别介

绍其影响因素和调控方法(表 5)。

丝网印刷指的是将墨水通过丝网微孔结构均匀转印到衬底上, 进而结晶成膜的方法。对于丝网印刷, 网格形貌和墨水黏度是最关键的影响因素(图 8a)。Raminafshar 等^[131]研究了网格尺寸对薄膜形貌的影响, 实验表明网格尺寸和螺距越大, 制备的薄膜也就越厚。和其他印刷方法一样, 衬底温度对薄膜以及器件性能也有显著的影响。Martinez 等^[132]探究了 30 °C 到 90 °C 的衬底温度对印刷效果的影响效果, 发现当衬底预热至 60 °C 时印刷制备的钙钛矿薄膜性能最佳, 展现了最高的器件效率。钙钛矿前驱体墨水的黏度同样会影响沉积膜的形貌。Chen 等^[21]发现当钙钛矿墨水黏度增加时, 其在网孔间的流动性会相应减弱, 钙钛矿薄膜的厚度也就会随之减小。添加剂工程也是提高丝网印刷钙钛矿薄膜质量的常用策略。Ri 等在墨水中加入了聚乙二醇(PEG), 发现该添加剂能有效增大钙钛矿晶体的尺寸, 从而减少界面的载流子复合, 进而提高钙钛矿薄膜的光吸收能力, 并实现了 14.71% 的器件

PCE^[133]。Kim 等则在墨水加入了醋酸钴, 可以提高钙钛矿的结晶度和光吸收性能, 器件的最高 PCE 为 14.89%^[134]。

喷涂法指的是利用超声振动等方式将墨水雾化并且均匀分散在衬底上, 进而结晶成膜的方法。喷涂法的影响因素主要包括喷雾流量、超声频率、墨水成分等。Heo 等^[135]指出控制溶剂挥发和雾滴沉降的平衡是喷涂法制备钙钛矿液膜的关键, 他们还发现当 DMF 和 GBL 的体积比为 8:2 时, 钙钛矿湿膜

中的溶解-再结晶过程进行地更加充分, 其活性面积为 40 cm² 的模组 PCE 达到了 15.5%(图 8b)。Huang 等^[136]则发现两步法同样也能通过喷涂法来实现, 制备的薄膜具有优异的结晶度和热稳定性、较弱的非辐射复合和更高效的界面电荷转移。Heo 等^[137]通过喷涂法制备了具有梯度结构的 CsPbI_{3-x}Br_x 钙钛矿薄膜。该梯度结构增大了材料的光吸收范围, 延长了载流子寿命, 可以实现更有效的电荷分离和提取, 开孔面积为 112 cm² 的子模组 PCE 可达 13.82%。

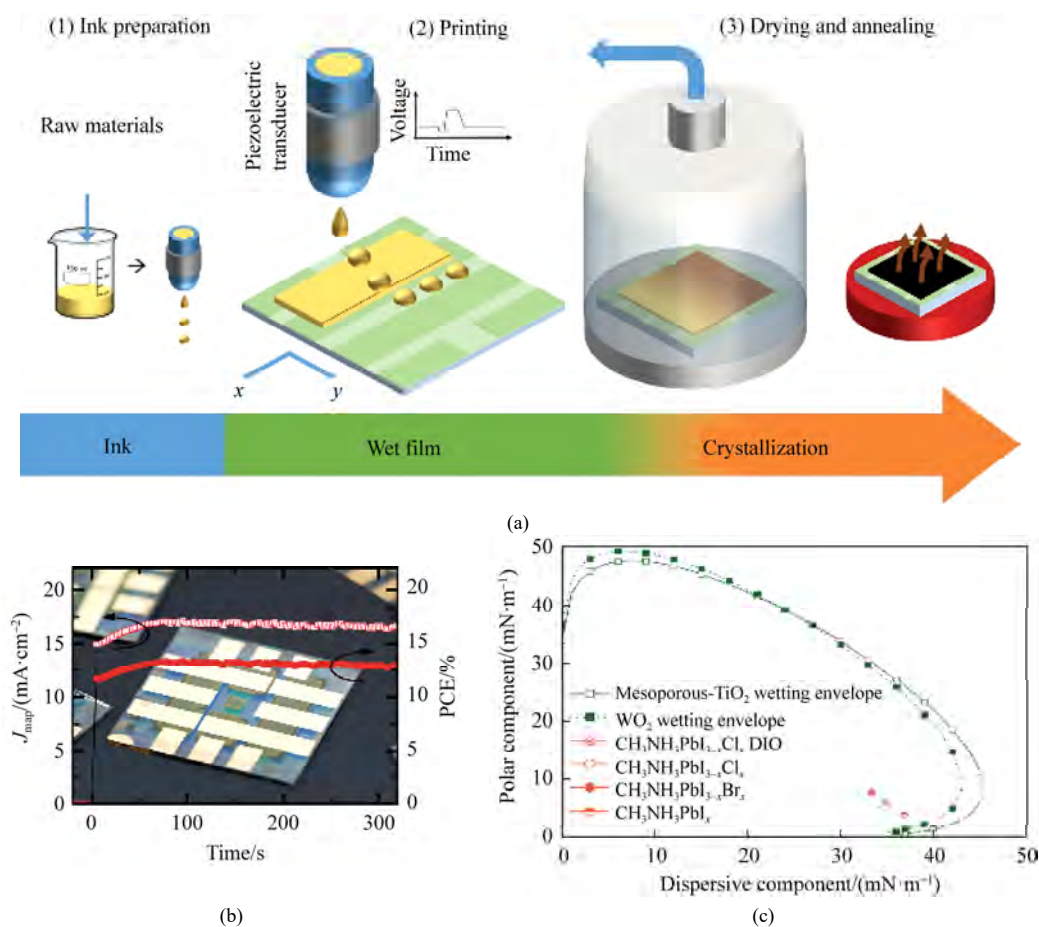


图 7 (a)三阳离子多晶钙钛矿(TCP)薄膜喷墨打印关键步骤示意图^[51]; (b)喷墨打印钙钛矿太阳能电池的实物照片^[128]; (c)各种钙钛矿墨水的润湿性^[129]

Fig. 7 (a) Schematic diagram of the key steps of triple cation polycrystalline perovskite (TCP) thin film inkjet printing; (b) Photograph of PSCs fabricated by inkjet-printing method; (c) Wettability of various perovskite inks

表 5 其他方法制备活性面积不小于 1 cm² 器件的处理方法和参数表

Table 5 Processing methods and parameters of devices with active area not less than 1 cm² prepared by other methods

Device structure	Power conversion efficiency/% (R/F)	Area/cm ²	Area type	Certified	Process	Reference
FTO/c-TiO ₂ /m-TiO ₂ /ZrO ₂ /FA _{0.15} MA _{0.85} PbI ₃ /C	11.8*	16.37	Active	No	Add methyl ammonium acetate ionic liquid	[21]
FTO/TiO ₂ /MAPbI _{3-x} Cl _x /PTAA/Au	15.5*	40	Active	No	Control solvent evaporation rate	[135]
FTO/bi-TiO ₂ /Graded CsPbI _{3-x} Br _x /PTAA/Au	13.82*	112	Active	No	Achieve gradient structured perovskite	[137]
FTO/Dense-TiO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro-OMeTAD/Au	13.09*	1	Active	No	Modify two-step deposition strategy	[136]

Note: * after PCE indicates that only the highest efficiency is provided without indicating forward or reverse scanning.

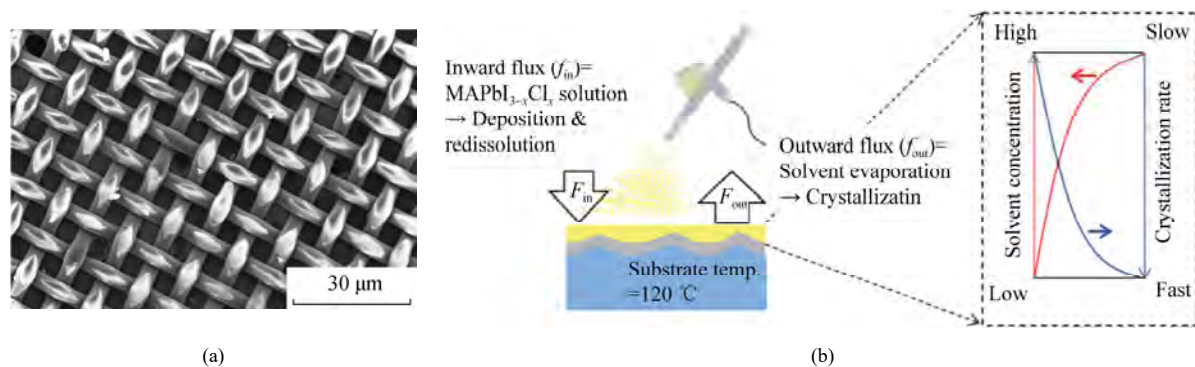


图 8 (a)丝网的 SEM 照片^[131]; (b)喷涂法雾滴蒸发和雾沉积的原理示意图^[135]

Fig. 8 (a) SEM image of the screen^[131]; (b) Scheme diagram of the inward flux of the spray solution and the outward flux of the evaporating solvent during spray coating^[135]

3 研究现况和挑战

PCE 是各印刷方法应用效果的最直观体现。图 9 为各印刷方法制备器件的 PCE 与器件面积相互关系图。由图 9 可见, 对于刮涂, 目前大多数报道已经能实现 25 cm^2 以下的模组制备, 虽然 PCE 已达 22%左右的水平, 却仍鲜有工作制备超过 75 cm^2 的光伏模组。对于狭缝涂布已有许多研究报道了面积大于 50 cm^2 的模组, 充分展示了该方法在大面积太

阳能制备上的可行性, 相比刮涂法和狭缝涂布法, 其他方法的相关报道非常少, 且器件的 PCE 水平也相差很多。在计量棒涂布、喷墨打印、丝网印刷以及喷涂法 4 种印刷方法中, 仅喷墨打印报道了超 20% 的 PCE, 其他方法制备的器件 PCE 都非常有限。即便如此, 真正通过喷墨打印实现的高效大面积钙钛矿模组也依然鲜有报道。可见除刮涂和狭缝涂布外, 其他方法虽都能实现大面积钙钛矿光伏的制备, 却仍难实现高效大面积器件的制备。若进一

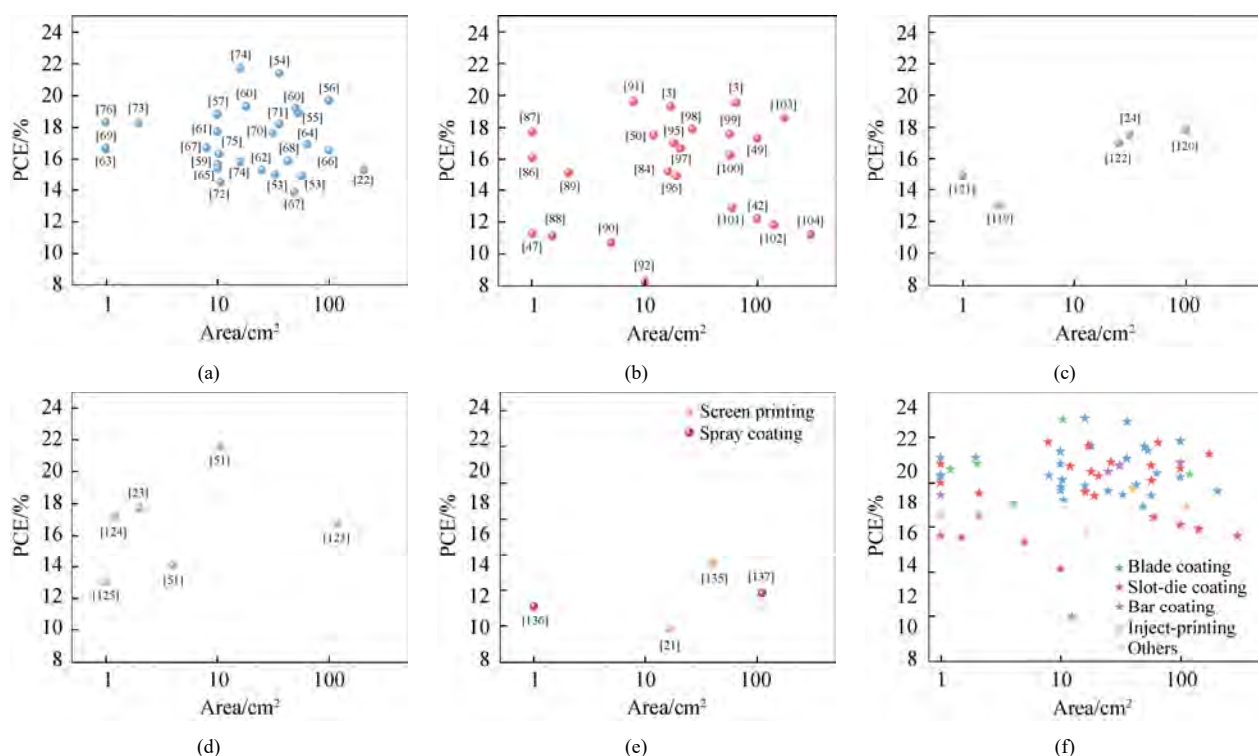


图 9 (a)刮涂、(b)狭缝涂布、(c)计量棒涂布、(d)喷墨打印、(e)丝网印刷和喷涂法制备器件(报道面积不小于 1 cm^2) 的 PCE 和与面积关系; (f)各种印刷技术制备器件的 PCE 与面积关系

Fig. 9 Relationship between PCEs and area of modules (reported area $\geq 1 \text{ cm}^2$) fabricated by (a) blade-coating, (b) Slot-die coating, (c) Bar-coating, (d) Inject-printing and (e) screen-printing and spray-coating; (f) Relationship between PCEs and area of modules fabricated by different printing methods

步考虑到薄膜均匀性和工艺可控性,显然狭缝涂布法又比刮涂法展现出了更多优势,因此狭缝涂布是目前最有潜力应用于产业化的印刷技术。

即使目前研究者们已在大面积制备和高效率制备等方面取得了一些开创性的成果,大面积印刷技术距离实际的产业化仍存在着较大差距,以下分别讨论:

首先是器件性能方面。大面积钙钛矿光伏的 PCE 仍有较大的提升空间^[8]。目前大多数模组的 PCE 仍难以超过 20%,和小面积近 26%的 PCE 存在着巨大的差异。如何进一步改善钙钛矿薄膜印刷技术,进而实现更高的 PCE 和器件稳定性将是下一阶段必须解决的问题。通过印刷方法大面积制备其他功能层也是真正实现大面积的高效钙钛矿光伏的必要条件。目前,已有一些研究报道了部分印刷或全印刷的钙钛矿光伏技术^[34–35, 62, 83, 129, 133–134],但这些功能层的印刷技术仍处于起步阶段,其影响因素和调控方法仍有待进一步探究和优化。

其次是工艺设计方面。为实现高效模组,除了需要优化各层材料外,还需要开发出先进的模组加工技术。其中,激光刻线技术将是影响模组性能的关键^[138–142]。如果激光刻线区域过宽,则模组的几何填充因子(GFF)就会减小,进而降低面积空间的利用率。此外,如果刻蚀深度或宽度不够,残留物清除不干净,则会增大子电池间的电阻,阻碍载流子的传输。因此,细而深度合适的激光刻蚀既能充分利用模组的面积发电,又能不阻碍电荷在各层间的迁移,即兼顾空间利用率和性能优越性。

最后是产速和成本方面。目前鲜有研究深入关注钙钛矿模组的生產速度,也基本没有研究报道能兼顾高产速和优性能的大面积钙钛矿制备方法,这将是未来研究者们非常值得填补的空缺^[14–15]。此外,目前鲜有报道准确而系统地分析包括仪器成本、药品和耗材成本、以及操作成本在内的印刷成本,并系统分析印刷技术的经济性。在保证模组 PCE 高和稳定性强的基础上,进一步缩减模组的制备成本并提高生产速度将直接大幅推进钙钛矿的商业化,也是一项非常有意义的挑战。

4 总结与展望

制备高品质的大面积钙钛矿薄膜,是实现钙钛矿光伏规模化的必要条件。目前先进的印刷技术主要包括操作简单但均匀性有限的刮涂法、能控速供液的狭缝涂布法、非接触涂布但速度较慢的喷墨打

印法、能直接应用于卷对卷生产的计量棒涂布法、操作简单的丝网印刷法以及制膜均匀的喷涂法等。对这些印刷技术,改善印刷工艺和调控墨水成分是最重要的 2 种调控方法,其最终目的都是调控结晶和相变的热动力学,进而实现高效大面积钙钛矿模组的制备。

在印刷工艺方面,各印刷方法的影响因素互不相同。对于刮涂,弯液面的状态直接影响着铺展液膜的均匀性,因此可以通过调节刮刀和衬底间距、刮涂速度等方式来调控结晶速度和薄膜均匀性;对于狭缝涂布,其薄膜质量与给液动力学密切相关,墨水供速和刀头移速均会影响薄膜厚度;对于计量棒涂布法,在制备过程中的涂布时间、衬底温度、涂布溶液的黏度和浓度等均会对成膜产生影响,因此调控这些参数非常重要;对于喷墨打印,可以通过喷嘴和衬底的间距或打印层数来控制钙钛矿薄膜的晶体厚度,也可以通过调控液滴的几何排列来优化液膜的均匀性;对于丝网印刷,网格尺寸直接影响着钙钛矿薄膜的形貌和厚度,因此设计合适的孔径和螺纹对实现钙钛矿薄膜的均匀性和致密性有着非常重要的意义;对于喷涂法,喷雾流量、超声频率、墨水成分都是重要的影响因素,可以针对性地调控这些参数,从而优化液滴的分散过程和钙钛矿薄膜的均匀性。此外,衬底预热、吹气辅助或反溶剂辅助也都是常见的外界热力学调控策略,可以加速结晶体系的形核速度,从而实现更致密的薄膜形貌。在干燥和退火方面,除了常见的热传导式加热外,还有真空淬火、NIR 退火和高能光线退火等策略同样能达到除去溶剂和熟化的效果。

除了工艺上的调控外,墨水成分的调控也是实现高质量薄膜的关键途径。溶剂的性质在极大程度上影响了大面积印刷技术的成膜过程^[143]。对于刮涂法和狭缝涂布法,溶剂本身的挥发速率和黏度在很大程度上影响着弯液面铺展液膜的均匀性;对于计量棒涂布法,过低的墨水黏度会导致液膜铺展不均匀的问题,而黏度较高的溶剂往往干燥较慢,钙钛矿过度的生长就会使薄膜晶粒间产生孔洞。因此,可以通过 MA 气体和钙钛矿晶体反应的策略直接制备高黏度且易干燥的墨水,也可以通过引入添加剂等方法加快形核速度;对于丝网印刷法,溶液黏度越大,流动性越差,制备的薄膜也就越薄,因此可以通过调控溶液的黏度来控制钙钛矿薄膜的厚度;对于喷墨打印,为避免喷嘴堵塞就必须选用高沸点且不易挥发的溶

剂, 为形成均匀的液滴又只能选用低黏度的溶剂, 因此在溶剂的选择上存在着限制; 对于喷涂法, 溶液的浓度和挥发性都直接影响着钙钛矿的结晶速度, 进而影响着薄膜的形貌。特别地, 添加剂也是改善结晶过程的常用策略, 许多添加剂都能和钙钛矿或钙钛矿前驱体结合或反应形成中间相, 调节结晶过程, 进而调控钙钛矿薄膜的结构与形貌, 若带有 Lewis 酸或 Lewis 碱的官能团, 则还能进一步钝化钙钛矿晶体的缺陷。此外, 还有一些添加剂能通过配位物或中间相的形式改变相转变的热动力学, 一方面能减小前驱体转变为有光伏效应钙钛矿相的势垒; 另一方面能优化钙钛矿薄膜和器件的稳定性, 也值得未来进一步探究。

根据目前的研究, 狭缝涂布法凭借其易调控的结晶热动力学、高 PCE 等诸多优势从多种印刷技术中脱颖而出, 并在柔性器件和卷对卷生产方面展现了广阔的应用前景^[14, 16]。因此, 钙钛矿的大面积印刷技术会更加多元和高效, 同时能兼顾低成本和高通量制备的优势, 从而使钙钛矿光伏能真正实现高 PCE 和大面积的产业化要求。

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蒋瑞轩，武汉理工大学材料复合新技术国家重点实验室在读博士研究生，主要从事材料科学和新型薄膜太阳能电池研究。



卜童乐，武汉理工大学材料复合新技术国家重点实验室研究员，博士生导师，主要从事材料科学和新型薄膜太阳能电池研究。在材料、化学、能源及其交叉学科领域发表学术论文 40 余篇，包括 *Science*, *Nature Energy*, *Nature Communications* 等。担任《物理化学学报》、《eScience》期刊青年编委。



黄福志，武汉理工大学材料复合新技术国家重点实验室研究员，博士生导师，主要从事材料科学和新型薄膜太阳能电池研究。入选 RSC 英国皇家化学学会能源与可持续大类期刊 2019 年全球 Top 1% 高被引作者，并获得 2019 IAAM Medal Award，湖北省“有突出贡献中青年专家”荣誉称号。在 *Science*, *Nature* 等期刊发表学术论文 100 余篇。担任中国材料研究学会太阳能分会专业委员会委员、中国能源学会新能源专家组成员、以及国际学术期刊《Crystals》和《Interdisciplinary Materials》编委。