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Recent developments in perovskite-based precursor inks for scalable architectures of perovskite solar cell technology

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The progressive enhancements in solar-to-electrical conversion within the past decade have allowed organic–inorganic lead halide perovskite-based solar cell (PSC) technology to become a competitive candidate for creating affordable and sustainable electricity. This review highlights the developments in fabricating advanced precursor inks of organic–inorganic lead halide perovskite-based light harvesters for large-area perovskite solar cell technology. One of the key characteristics of this promising photovoltaic technology includes solution processing, which offers possibilities to scale up lab-sized solar cell devices into large-area perovskite solar modules comprising unique device architectures. These have been realized in recent years for their deployment in various applications such as building-integrated photovoltaics or internet of things (IoT) devices. In this regard, the presented overview highlights the recent trends that have emerged in the research and development of novel perovskite precursor ink formulations, and it also discusses their contribution toward demonstrating efficient, scalable, and durable PSC technology to create electricity and energize futuristic applications. Various

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reports were included aiming to showcase the robust photovoltaic performance of large-area perovskite solar modules in a variety of device configurations, hence providing a brief overview of the role of state-of-the-art scalable precursor ink development in transforming unstable lab-sized solar cells into robust, low-cost perovskite solar cell technology that can be scaled up to cover much larger areas.

1. Introduction

Since its first report,¹ the rapid escalation of solar-to-electrical conversion over the last decade (Fig. 1)^{1–10} has made organic–inorganic lead halide perovskite-based solar cell (PSC) technology a game-changer for creating electricity at an affordable cost.¹¹ Its key features include solution processing, which offers the possibility of rapid production of perovskite solar modules (PSMs), efficient solar-to-electrical energy conversions under various light intensity conditions,^{12,13} and the well-established long term operational stability under various environmental

conditions.^{12,14–18} Thus, PSC technology has become a unique candidate among other emerging and next-generation-based photovoltaic (PV) technologies^{19–22} in the emerging area of building-integrated photovoltaics (BIPV)²³ and for the next generation of maintenance-free IoT devices.^{24–26}

This review highlights the developments being made in the fabrication of advanced scalable precursor inks of organic–inorganic lead halide perovskite-based light harvesters for large-area PSC technology. In the past decade of progressive research, various scalable configurations for PSC technology have been developed.^{27,28} These have utilized various unique



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Marandi. Her research interests include nanostructures, solar cells, photovoltaics, semiconductors, photocatalysts, hydrogen evolution, synchrotrons, and materials characterization.



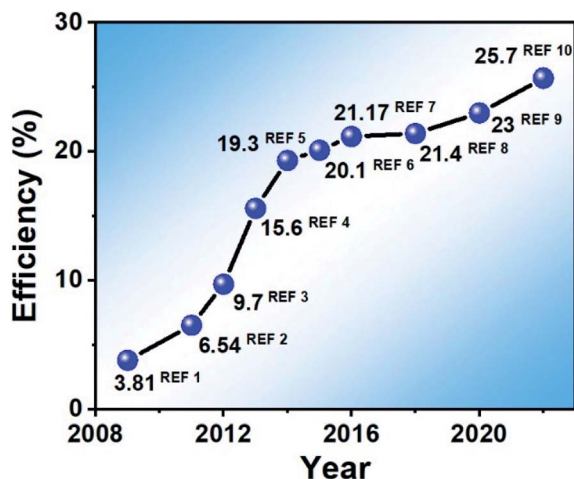


Fig. 1 Solar-to-electrical conversion efficiency evolution of lab-sized perovskite solar cells.

and advanced perovskite precursor inks for achieving efficient large-area PSCs and modules^{29,30} while demonstrating striking stability when tested under both simulated and natural environmental conditions.^{16–18} This report summarizes the trends that have emerged during the research and development of producing scalable perovskite precursor ink formulations, and it also discusses their contribution toward efficient, scalable, and durable PSC technology.



Jingshan Luo is a full professor and vice director of the Institute of Photoelectronic Thin Film Devices and Technology at Nankai University. He received his BSc degree from Jilin University in 2010 and his PhD degree from Nanyang Technological University in 2014. After that, he went to École Polytechnique Fédérale de Lausanne (EPFL) in Switzerland for post-doctoral research in the laboratory of Prof. Michael Grätzel, where he led the solar fuel subgroup.

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Prof. Ana Flávia Nogueira obtained her bachelor's degree in Chemistry from the University of São Paulo (1996) and master's (1998) and PhD degrees in Chemistry from the University of Campinas (2001). She worked as a post-doctorate fellow at Imperial College, UK (2001–2002) and as a visiting researcher at Stanford University (2017–2018). At the moment, Ana Flávia is a Full Professor in the

Chemistry Institute at UNICAMP and Director of the Center for Innovation on New Energies (CINE, <https://www.cine.org.br>). Prof. Nogueira's research focuses on the development of functional (nano)materials and their application in solar energy conversion. She has experience in the field of perovskite solar cells, perovskite quantum materials and dense energy carriers (generation of solar fuels through photoelectrocatalytic systems using water, CO₂ and other low added value substrates). She has published more than 170 papers, seven book chapters, one book and 3 patents. Her h-index is 40. The Laboratório de Nanotecnologia e Energia Solar (L NES) founded in 2005 has leadership in dye sensitized organic solar cells and perovskite solar research in Brazil and Latin America. In 2020 she was awarded the ACS Leadership in Academia Award.



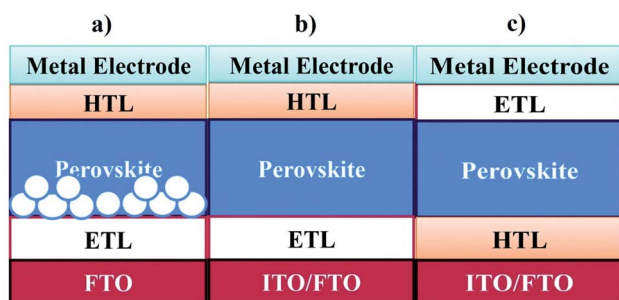


Fig. 2 Three fundamental and scalable configurations: (a) mesoporous n-i-p, (b) planar n-i-p, and (c) planar p-i-n, which have been reported for scaling-up during the emergence of perovskite solar cell technology in recent years (reproduced from ref. 31 with permission from the Royal Society of Chemistry).

2. Approaches for scaling-up various device designs of perovskite solar cell technology

The solution processing associated with individual layers of perovskite solar cells (PSCs) greatly influenced the scaling-up of technology from lab-sized devices to large-area modules, which have been fabricated on a variety of substrates.^{32–38} In this

regard, numerous configurations^{39–42} initially designed to produce lab-sized PSC devices have also been explored to scale-up the technology.^{43–46} Notably, three fundamental configurations (mesoporous n-i-p, planar n-i-p, and planar p-i-n) have emerged as the most applied in the scaling-up of PSCs (Fig. 2).

Motivated by the solid-state dye-sensitized solar cell (ss-DSSC) configuration,^{22,47,48} perovskite sensitized-based lab-sized solid-state solar cells were initially reported,^{43,49–51} now known as the mesoporous n-i-p perovskite solar cell device design (Fig. 2a). In this structure, the TiO₂-based electron transporting layers (ETLs) are achieved by first fabricating the compact layer (~5–70 nm in thickness) either by spray pyrolysis,^{52–56} spin coating^{44,45,49,57,58} or atomic layer deposition (ALD)^{59–63} on the desired substrates. After that, an additional mesoscopic layer of TiO₂-based ETL is fabricated either by spin coating or screen-printing^{64–68} processes before depositing the perovskite-based light-absorbing layers, hole transporting layer (HTL), and metal contacts (Table 1).

Nevertheless, the mesoporous TiO₂ has been systematically removed from the mesoporous n-i-p device design, for the following reasons: (1) achieving low temperature and binder-free based ink or paste formulations of nanoparticles based on TiO₂ has remained challenging when attempting to achieve scalable mesoporous n-i-p-based configurations on flexible polymer substrates. (2) The additional step of fabricating



Trystan Watson is a Professor in Photovoltaics and Director at the SPECIFIC Innovation and Knowledge Centre. After completing an undergraduate Chemistry Degree and Engineering Doctorate in Steel Technology at Swansea University, Prof. Trystan moved to Corus Strip Products (now Tata Steel) as a product development engineer and a theme leader for the process technology group in the

engineering doctorate scheme. In 2007, Prof. Trystan returned to academia to take up a research position in the development of dye-sensitized solar cells on metal substrates. Since then his research has focused on thin film printed PVs with a specialism in developing new technologies for the manufacture of solution processable photovoltaics such as perovskites and OPVs including deposition (roll-to-roll and sheet-to-sheet) and curing processes and their characterisation using electrochemistry, photochemistry and optoelectronic methods. He currently leads PV research at SPECIFIC and his research goal is to take new photovoltaic materials and develop the manufacturing pipeline for fabrication at scale. During his career, Prof. Trystan has published over 150 academic papers and is a chartered engineer with the IOM3 and a fellow of the Royal Society of Chemistry. Trystan is married with three daughters and a son and spends most of his home life wrapped around their fingers.



Syed Ghufuran Hashmi is a Tenure Track Assistant Professor in Printed Electronics at the Microelectronics Research Unit of the University of Oulu, Finland. He has received numerous prestigious funds in the capacity of Project Leader and Principal Investigator from top funding organizations including Technology Industries of Finland Centennial Foundation, Jane and Aatos Erkko

Foundation, Business Finland and Academy of Finland for the research and development of next-generation photovoltaic devices such as dye-sensitized solar cells and perovskite solar cells. He received his DSc degree in Engineering Physics from Aalto University – Finland in 2014. Before that, he received his MSc degree in Micro- and Nanotechnology from Helsinki University of Technology – Finland in 2009 and BS degree in Biomedical Engineering from Sir Syed University of Engineering and Technology – Pakistan in 2002. He has authored nearly 30 scientific publications, which have received 1120+ citations. His research interests include solar cells, printed electronics, energy harvesting, solar fuels, printable batteries and supercapacitors.





Table 1 Overview of the scalable perovskite solar cell device designs that have been reported in recent years

| Deposition method | | ETL | HTL | Structure | Architecture | Contacts | Precursor ink | Area (active area cm ²) | PCE (%) | Substrate | Year | Ref. |
|--|-------------------------------|----------------------------|--------------|---------------------|--------------|----------|---|-------------------------------------|-------------------------------|----------------------|------|------|
| Perovskite | Spin-coating | Spin-coating | Spin-coating | Modules | p-i-n | LiF/Al | CH ₃ NH ₃ I and PbI ₂ were stirred in a mixture of DMSO : GBL (3 : 7, v/v) | 10 × 10 (60) | 8.7% @ 1 sun | ITO-glass | 2014 | 95 |
| Spin-coating | Screen-printing | Spin-coating | Modules | Mesoporous n-i-p | Au | Au | CH ₃ NH ₃ I and PbCl ₂ (molar ratio 3 : 1) in DMF | 5 × 5 (16.8) | 5.1 @ 1 sun | FTO-glass | 2014 | 96 |
| Spin-coating | Spray pyrolysis | Spin coating | Modules | 10 sub- p-i-n units | Au | Au | MAPbI ₃ solution (40 wt%) was prepared by mixing the MAI powder and PbI ₂ (1 : 1 mole ratio) in DMF | 10 × 10 (40) | 12.9 @ 1 sun | FTO-glass | 2015 | 97 |
| Slot-die coating | Slot-die coating | Slot-die coating | Modules | n-i-p | Ag | Ag | PbI ₂ (322 mg mL ⁻¹ in DMF) and CH ₃ NH ₃ I (10 mg mL ⁻¹ in 2-propanol) | 10 × 10 (40) | 11.96 @ 1 sun | ITO-glass | 2015 | 98 |
| Dropping by micropipette | Screen-printing | — | Modules | n-i-p | C | C | The equimolar ratio of PbI ₂ and CH ₃ NH ₃ I in γ -butyrolactone | 10 × 10 (70) | 10.74 @ 100 W white light LED | FTO-glass | 2016 | 99 |
| Spray coating | Spray pyrolysis | Spin coating | Modules | n-i-p | Au | Au | Mixed solution of DMF (dimethylformamide) : γ -butyrolactone (GBL) (v/v) to prepare the 0.8 M MAPbI _{3-x} Cl _x | 10 × 10 (40) | 15.5 @ 1 sun | FTO-glass | 2016 | 100 |
| Dipping PbI ₂ substrates into MAI in IPA solution | Spray pyrolysis/ spin coating | Air assisted blade-coating | Modules | Mesoporous n-i-p | Au | Au | PbI ₂ substrates and MAI in IPA solution (10 mg mL ⁻¹) | 10 × 10 (50) | 12.6 @ 1 sun | FTO-glass | 2017 | 101 |
| Pressure processing | Spin coating | Spin coating | Single-cell | Mesoporous n-i-p | Au | Au | CH ₃ NH ₃ I·3CH ₃ NH ₂ and PbI ₂ ·CH ₃ NH ₂ , in a molar ratio of 1 : 1; | 8 × 8 (36.1) | 12.1 @ 1 sun | FTO-glass | 2017 | 102 |
| Vapor-solid reaction method | Soaking and heating | Spin coating | Modules | n-i-p | Au | Au | CH ₃ NH ₃ I·3CH ₃ NH ₂ and PbI ₂ ·CH ₃ NH ₂ precursors were prepared by inducing CH ₃ NH ₂ gas | 8 × 8 (41) | 12.24 @ 1 sun | FTO-glass | 2018 | 50 |
| Megasonic spray-coating | Thermal evaporation | Spin-coating | Single-cell | p-i-n | Cu | Cu | Cs _x FA _{1-x} PbI _{3-y} Br _y | 7.5 × 7.5 (18) | 16.9 @ 1 sun | ITO-glass | 2018 | 57 |
| Inkjet printing | Spin coating | Spin-coating | Single-cell | Mesoporous n-i-p | Au | Au | 400 mg mL ⁻¹ PbI ₂ in DMF/ DMSO (volume ratio = 1 : 1) and MAI powder | ~3.1 × 3.1 (2.02) | 17.74 @ 1 sun | FTO coated substrate | 2018 | 39 |
| Spin coating | Spin coating | Spin coating | Single-cell | n-i-p | Ag | Ag | [CsPbI ₃]0.05[[FAPbI ₃]0.85(MAPbBr ₃]0.15][0.95 in DMSO/DMF with a 5% molar ratio PbI ₂ excess | 14 × 14 (1.08/ 2 × 2 cell) | 17.39 @ 1 sun | FTO-glass | 2018 | 45 |



Table 1 (Contd.)

| Deposition method | | HTL | | Structure | Architecture | Contacts | Precursor ink | Area (active area cm ²) | PCE (%) | Substrate | Year | Ref. |
|----------------------------------|------------------|------------------|------------------|----------------------|--------------|----------|---|--|------------------------------|-----------|------|------|
| Perovskite | ETL | Bar-coating | Spin coating | Modules | n-i-p | Au | MAI and PbI ₂ at an equimolar ratio were dissolved in mixed NMP : DMF (9 : 2) | 8 × 10 | 17.28 @ 1 sun | ITO-glass | 2019 | 103 |
| Blade-coating | Spin coating | Spin coating | Spin coating | Single-cell | n-i-p | Au | 461 mg of PbI ₂ , 78 mg of DMSO, and 159 mg of MAI dissolved in 600 mg of DMF and 0.05% ZnP | 4 × 4 | 20.5 @ 1 sun | FTO-glass | 2019 | 44 |
| Air-knife-assisted D-bar coating | Spin coating | Spin coating | Spin coating | Single-cell | n-i-p | Au | 0.12 mmol GAI, 1.78 mmol MAI, 0.7 mmol PbI ₂ (10 mol% PbI ₂ excess) and 0.4 mmol PbAc ₂ were dissolved in 1 mL 2-ME | 4.8 × 9.6 (16) | 13.85 @ 1 sun | FTO-glass | 2019 | 104 |
| Solution-bathing | Spin coating | Spin coating | Spin coating | Single-cell | p-i-n | Au | PbI ₂ (1.15 M), FAI (1.09 M), PbBr ₂ (0.20 M), MABr (0.14 M) and CsI (0.06 M) in a mixed solvent of DMF/DMSO/NMP (DMF/DMSO, 4/1, v/v) | 5 × 5 (1.00) | 18 @ 1 sun | ITO-glass | 2020 | 58 |
| D-bar coating | Spin coating | Spin coating | Spin coating | Modules 10 sub-cells | n-i-p | Au | Dissolving 553.8 mg of the FAPbI ₃ powder, 26.6 mg of CsBr, 45.8 mg of PbBr ₂ , and 20.4 mg of MACl in 700 µL DMF or HMPA; for the Lewis base additive, 0.6 mmol DMSO or 0.6 mmol HMPA was included in the precursor solution | 5 × 5 (18.66) | 17.01 @ 1 sun | FTO-glass | 2020 | 43 |
| Spin-assisted solvent extraction | Spin coating | Spin coating | Spin coating | Modules | n-i-p | Ag | An equal amount of MAI and PbI ₂ (or FAI, MAI, and PbI ₂ mixture or FAI, MAI, PbI ₂ , and PbBr ₂ mixture) was dissolved in 2P to make a precursor solution with a concentration of 1.5 M | 10 × 10 (25.2) | 14.36 @ 1 sun | ITO-glass | 2020 | 105 |
| Slot-die coating | Slot-die coating | Slot-die coating | Slot-die coating | Single-cell/modules | p-i-n | Ag | 276 mg PbI ₂ , 96 mg MAI, and 0.18 mg PEG were dissolved in the solvent mixtures of GBL and DMSO | 2 × 2 (0.09; cut from 12 × 12)/4 × 4(3.78) | 11 @ 1 sun/ 10.34 @ 1 sun | FTO-glass | 2020 | 106 |

Table 1 (Contd.)

| Deposition method | | ETL | HTL | Structure | Architecture | Contacts | Precursor ink | Area (active area cm ²) | PCE (%) | Substrate | Year | Ref. |
|---|--------------------------|---------------------|-----|-----------|--------------|----------|--|-------------------------------------|----------------|-----------|------|------|
| Perovskite | | | | | | | | | | | | |
| HPNE strategy assisted slot-die coating | Chemical bath deposition | Spin coating | HTL | Modules | n-i-p | Au | FA _{0.91} Cs _{0.09} PbI ₃ perovskite precursor was prepared in a mixed solvent (DMF : DMSO = 4.75 : 1) with a concentration of 1.25 M, 23 mol% MACl was added | 0.6 × 3.4 × 5-sub-cell (10.2) | 18.6 @ 1 sun | FTO-glass | 2020 | 41 |
| Slot-die method | Slot-die method | Slot-die method | | Modules | n-i-p | Cr/Au | 553.2 mg PbI ₂ and 15.6 mg CsI were dissolved in 0.9 mL DMF and 0.1 mL DMSO; 75 mg FAI and 2.5 mg FACl were dissolved in 1 mL isopropanol | 8 × 8 (35.80) | 15.3% @ 1 sun | FTO-glass | 2021 | 107 |
| Spin-coating | Spin-coating | Spin-coating | | Modules | n-i-p | Au | 2.2 M PbI ₂ and 28 mg CsI were dissolved in 1 mL DMF solution with different molar ratios of NH ₄ Cl (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0 M) | 10 × 10 (91.8) | 10.25% @ 1 sun | ITO-glass | 2021 | 108 |
| Spin-coating | Chemical bath deposition | Thermal evaporation | | Modules | n-i-p | Au | 1.35 M PbI ₂ and 0.0675 M CsI were dissolved in a mixed solution (1.9 mL DMF and 0.1 mL DMSO); FAI 1000 mg; MAI 110 g; MABr 110 mg; MACl 110 mg, dissolved in 15 mL IPA | 10 × 10 (91.8) | 21.70% @ 1 sun | FTO-glass | 2021 | 109 |
| Spin-coating | Spin-coating | Spin-coating | | Modules | n-i-p | Au | Lead iodide (1.51 M), formamidine iodide (1.47 M), methylammonium bromide (0.03 M), lead bromide (0.03 M), and methylammonium chloride (0.6 M) in the mixed solvent of DMF : DMSO (8/1, v/v) | 10 × 10 (45.6) | 17.97% @ 1 sun | FTO-glass | 2022 | 110 |



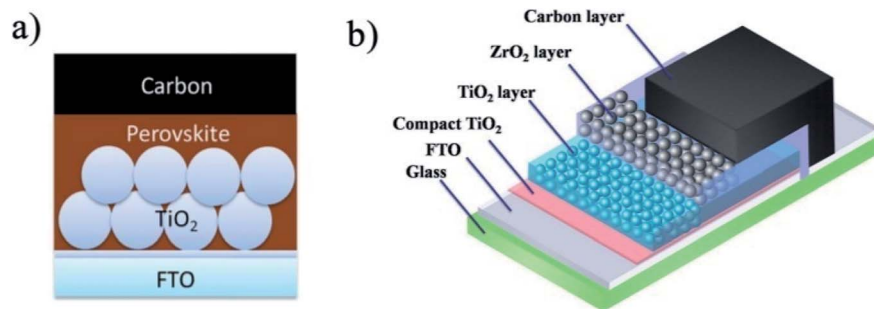


Fig. 3 Scalable carbon-based configurations. (a) Carbon-based perovskite solar cell (C-PSC) configuration (reproduced from ref. 93 with permission from the Royal Society of Chemistry). (b) C-PSC with a ZrO_2 spacer to keep the carbon layer separated from the photoanode (reproduced from ref. 94 with permission from the Royal Society of Chemistry).

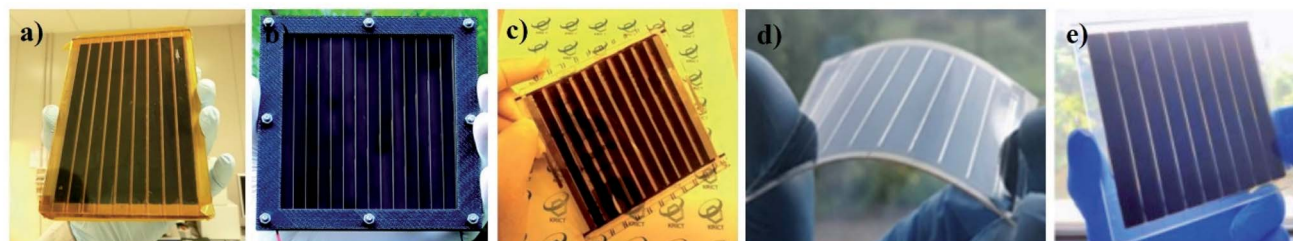


Fig. 4 Examples of various types of large-area perovskite solar modules fabricated on rigid and flexible substrates. (a) A mesoporous glass-based n-i-p solar module (reproduced from ref. 30 with permission from Elsevier, copyright 2022). (b) A planar n-i-p glass-based perovskite solar module (reproduced from ref. 111 with permission from the Royal Society of Chemistry). (c) An inverted p-i-n configured glass-based perovskite solar module (reproduced from ref. 95 with permission from the Royal Society of Chemistry). (d) An inverted p-i-n-based flexible solar module fabricated on PET polymer substrates (reproduced from ref. 112 with permission from the American Chemical Society). (e) A carbon-based triple-mesoscopic printable perovskite solar module on a rigid glass substrate (reproduced from ref. 66 with permission from Elsevier, copyright 2022).

a mesoporous TiO_2 -based ETL in the device structure induces additional cost and time, which may limit the competitiveness of the technology compared to other existing solutions.

As a result, the n-i-p-based planar structure (Fig. 2b) gained attention since it can achieve good solar-to-electrical conversion efficiencies upon removing the mesoporous ETL layers from the traditional n-i-p device design of PSCs. Moreover, inspired by the solution processing of organic solar cells,^{69–73} scaling-up schemes of PSC technology with a planar n-i-p device design have also been rapidly developed and demonstrated both on flexible polymers and rigid glass-based substrates.^{32,41,45,46,74,75}

Similarly, the inverted structure of the p-i-n device design (Fig. 2c) has also been realized recently because of the availability of a wide range of material-based ink formulations already tested in lab-sized devices as well as in large-area module configurations, with impressive solar-to-electrical conversion efficiencies (Table 1).

In contrast to these traditional configurations, other scalable device designs *i.e.*, HTM- and metal contact-free carbon-based perovskite solar cell configurations (Fig. 3) have also been reported in recent years.^{76–85} These novel device designs have emerged by first replacing the ruthenium dyes and liquid electrolytes from the monolithic DSSC configurations with a perovskite sensitizer.^{86–88} This strategy allowed a low-cost, printable, and solid-state device configuration that demonstrated impressive solar-to-electrical energy conversion combined with

exceptional stability when exposed to numerous simulated and natural climatic conditions.^{1,89–92} Table 1 provides an overview of the scalable perovskite solar cells produced in various device designs. Fig. 4 represents the actual demonstrations of perovskite solar modules produced in some of the most established configurations discussed earlier in this section.

3. Historical evolution of perovskite precursors tested for scalable perovskite solar cells and modules

The solution processing associated with active layers of PSC technology, including perovskite-based light-absorbing layers, has greatly motivated research groups worldwide to create their novel and scalable precursor solutions that could be integrated into scalable cell architectures *via* various scalable material deposition methods, such as blade coating, inkjet printing, slot-die coating, or spraying-based material deposition technologies.

One of the initial studies was reported by Matteocci and co-workers, who demonstrated the first scalable and fully solid-state n-i-p-based perovskite solar modules (PSMs) fabricated on rigid glass substrates.⁹⁶ Interestingly, the spin-coating technique was chosen for the perovskite precursor ink deposition, comprising a mixed halide solution in *N,N*-dimethylformamide



Table 2 Large-area modules were fabricated in recent years by employing scalable perovskite precursor inks

| Device structure | Perovskite precursor ink | Active area (cm ²) | PCE (%) | Year | Ref. |
|---|--|--------------------------------|---------|------|------|
| Glass/FTO/c-TiO ₂ /n-TiO ₂ /perovskite/P3HT/Au | Methylammonium iodide CH ₃ NH ₃ I and lead chloride PbCl ₂ in <i>N,N</i> -dimethylformamide, molar ratio 3 : 1 | 16.8 | 5.1 | 2014 | 96 |
| Glass/ITO/PEDOT : PSS/perovskite/PCBM/LiF/Al | The CH ₃ NH ₃ I and PbI ₂ were stirred in a mixture of DMSO : γ -butyrolactone (GBL) (3 : 7, v/v) at 60 °C for 12 h | 60 | 8.7 | 2014 | 95 |
| Glass/FTO/BL-TiO ₂ /perovskite/Spiro-OMeTAD/Au | The 0.6 mL per sample of CH ₃ NH ₃ PbI _{3-x} Cl _x perovskite precursor solution (40 wt%) was deposited by spin-coating at 2000 rpm for 60 s | 10.08 | 13 | 2016 | 114 |
| Glass/FTO/c-TiO ₂ /perovskite/Spiro-OMeTAD/Au | The typical recipe for 45 wt% precursor with 30% MACI additive is 0.2 g MAI, 0.580 g PbI ₂ , 0.025 g MACI, 0.524 g NMP and 0.429 g DMF | 11.09 | 14.06 | 2017 | 115 |
| PET/ITO/SnO ₂ /Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb _{(0.85Br_{0.15})₃/Spiro-OMeTAD-Au} | Dissolving 1.3 M organic cations (0.85 FAI and 0.15 MABr) and a 1.4 M mixture of metal lead salts (0.85 PbI ₂ and 0.15 PbBr ₂) in a solvent of DMF/DMSO (4 : 1, by volume), and then a 34 μ L CsI solution (pre-dissolved as a 2 M stock solution in DMSO) added | 16.07 | 14.89 | 2018 | 116 |
| Glass/FTO/c-TiO ₂ /mp-TiO ₂ /MAPbI _{3-x} Cl _x /Spiro-OMeTAD/Au | Different molar ratios of MACI/HPbI ₃ are deposited on substrates. After thermal annealing, the obtained films react with CH ₃ NH ₂ gas to form perovskite | 12 | 15.3 | 2018 | 117 |
| Glass/FTO/NiO/perovskite/DBL/G-PCBM/Ag | 424 mg FAI, 1.136 mg PbI ₂ , 49 mg CH ₃ NH ₃ Br, and 160 mg PbBr ₂ dissolved in 2.4 mL acetonitrile | 36.1 ^a | 15.6 | 2019 | 118 |
| PEN/ITO/mp-SnO ₂ /porous-ZSO ETL/(FAPbI ₃) _{0.95} (MAPbBr ₃) _{0.05} /Spiro-OMeTAD/Au | 1.26 mmol of PbI ₂ , 1.26 mmol of FAI, 0.06 mmol of MAPbBr ₃ , and 0.5 mmol of MACI in DMF/DMSO | 90 | 15.5 | 2020 | 119 |
| MgF ₂ /Willow glass/ITO/PTAA/MAPi-NH ₄ Cl/C ₆₀ /BCP/Cu | <i>l</i> - α -Phosphatidylcholine and methylammonium hypophosphite were added into \approx 1.45 M MAPbI ₃ /2-ME solution at a concentration of \approx 0.3 mg mL ⁻¹ and \approx 0.15 vol%, 6×10^{-3} M NH ₄ Cl was added to the precursor | 42.9 | 15.86 | 2020 | 120 |
| Glass/FTO/ZnO-ZnS/mp-TiO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro-OMeTAD/Au | 1 mmol of MAI, 1 mmol of PbI ₂ , and MACI (<20 mol% of MAPbI ₃) were dissolved in an 800 μ L solution of CH ₃ NH ₂ solution in ethanol, and 200 μ L of CAN | 12 ^a | 16 | 2020 | 121 |
| PEN/hc-PEDOT : PSS/NiO _x /perovskite/PCBM/Ag | 547 mg PbI ₂ , 46 mg PbBr ₂ , 150 mg FAI, 39 mg MAI and 0.02 wt% PU in 1.5 mL anhydrous DMF and 1.5 mL anhydrous DMSO | 15 | 16.15 | 2021 | 113 |
| Glass/FTO/c-TiO ₂ /mp-TiO ₂ /Perovskite/MW doped-PTAA/Au | FAPbI ₃ (1.47 M) and MAPbBr ₃ (0.18 M) precursor complexes in 1 mL of mixed DME/DMSO solvent and 0.05 M CsI | 42.8 | 17.05 | 2021 | 122 |
| Glass/FTO/TiO ₂ /perovskite/[M ₄ N]BF ₄ /Spiro-OMeTAD/Ag | The FA _{0.91} Cs _{0.09} PbI ₃ perovskite precursor was prepared in a mixed solvent (DMF : DMSO = 4.75 : 1) with a concentration of 1.25 M, 23 mol% MACI was added | 7.92 | 19.0 | 2020 | 123 |
| Glass/FTO/TiO ₂ /SnO ₂ /ink/BJ-GO/Spiro-OMeTAD/Cr/Au | 645.4 mg PbI ₂ and 18.2 mg CsI were dissolved in 0.9 mL DMF and 0.1 mL DMSO for the first deposited solution. 90 mg FAI and 4 mg FACl were dissolved in 1 mL isopropanol for the second solution | 35.8 | 15.3 | 2021 | 107 |

^a Aperture area.

(DMF) (Table 2) for the development of their $5 \times 5 \text{ cm}^2$ PSM. The fabricated modules containing two types of HTMs exhibited similar (5.1%) solar-to-electrical energy conversion when tested under full sunlight illumination. Nevertheless, the modules fabricated with the traditional HTM (*i.e.*, Spiro-OMeTAD) exhibited higher long-term stability by maintaining more than 60% of their initial efficiency after 335 hours, compared to the alternative poly(3-hexylthiophene-2,5-diyl) (P3HT) polymer-based PSMs, in which the conversion efficiency was reduced by about 80% of the initial value after 170 hours.

This preliminary demonstration motivated research labs worldwide to further develop novel precursors that could be integrated into the desired scalable device configurations of PSC technology through established large-scale material deposition methods. For example, Xu and co-workers demonstrated a novel perovskite precursor ink that was introduced in triple mesoscopic carbon-based printable solar modules.⁶⁶ The novel precursor ink used in their study contained 5-ammonium valeric acid (5-AVAI) as a perovskite crystallization retarding agent, in addition to methylammonium iodide (MAI) and PbI_2 , which were dissolved in γ -butyrolactone (GBL) solvent to attain the stable and compatible perovskite precursor ink formulation. As a result, successful fabrication of carbon-based PSMs was achieved by incorporating this novel precursor formulation through the slot-die coating technique over an aperture area of 80.55 cm^2 . This resulted in achieving a striking conversion efficiency (12.87%) with an active area of 60.08 cm^2 when recorded under full sunlight illumination.

Contrary to the precursor inks demonstrated in the fabrication of rigid glass-based PSMs, other novel precursor inks have also been developed to produce large-area flexible perovskite solar cells and modules.^{98,113} For example, Wang *et al.* recently reported a one-step perovskite precursor ink solution by dissolving PbI_2 , PbBr_2 , formamidinium iodide (FAI), MAI, and 0.02 wt% PU in 1.5 mL anhydrous DMF and 1.5 mL anhydrous dimethyl sulfoxide (DMSO) mixture solvent.¹¹³ This novel precursor ink was meniscus-coated on the pre-HTL coated ITO-PET substrate to fabricate a large-area flexible solar module that exhibited impressive (>16%) solar-to-electrical energy conversion when tested under full sunlight illumination.

On the other hand, Castriotta and co-workers developed a blade-coated scalable precursor ink of the perovskite light-absorbing layer to produce a flexible perovskite solar module on an ITO-PET substrate.¹¹² A $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based precursor ink was produced by dissolving CsI, PbBr_2 , FAI, and PbI_2 in 1 mL of *N*-methyl-2-pyrrolidone (NMP)/DMF solvent, which was deposited on the HTL-coated ITO-PET substrate with N_2 -assisted blade-coating, followed by heating ($100 \text{ }^\circ\text{C}$) for 45 minutes. With this inverted device design produced on an ITO-PET substrate, the flexible module also exhibited >10% power conversion efficiency (PCE) over a 15.7 cm^2 active area by exploiting blade deposition of the transporting layer and a stable double-cation perovskite (cesium and formamidinium, CsFA)-based light-absorbing layer. More impressively, outstanding light stability of the fabricated modules – over 1000 h, considering the recovery time ($T_{80} = 730 \text{ h}$) – was also demonstrated, thus reinforcing the potential of this low-cost

solution-based PV technology. Table 2 highlights some of the high-performing large-area modules that are being developed by incorporating scalable precursor inks of the perovskite-based light-absorbing layer.

4. Rheological characteristics of perovskite precursor inks and scalable coating methods for deposition of large-area perovskite precursors

Interestingly, the progressive transition not only induced innovativeness in scalable device designs, but also provided opportunities to develop advanced perovskite precursor inks *via* examining their rheological characteristics to facilitate the upscaling goals of PSC technology.

In this regard, various reports have frequently surfaced that highlight key rheological parameters (Fig. 5) such as contact angles, viscosity, density, surface tension, or boiling points of the fabricated perovskite precursor inks.^{15,29,124–131} Such interesting trends led to the demonstration of various scalable device architectures of PSC technology fabricated by employing scalable perovskite-based precursor ink formulations along with scalable coating methods.

For example, Huang *et al.* reported the formulation of a novel PbI_2 ink by mixing traces of MAI and polyurethane (PU) as an additive with PbI_2 in the DMF/DMSO solvent mixture.¹²⁹ This novel ink engineering strategy regulated one of the key factors of rheological properties (*i.e.*, the viscosity) and influenced the chemical stability of the fabricated PbI_2 ink. As a result, both the successful room temperature-based scalable deposition of PbI_2 layers and the complete scalable deposition of perovskite light absorbing layers under ambient conditions were demonstrated through the two-step processing approach. An impressive 11.07% solar-to-electrical conversion efficiency was achieved for a 25 cm^2 based large-area perovskite solar module (PSM) when configured in a p-i-n based inverted configuration.

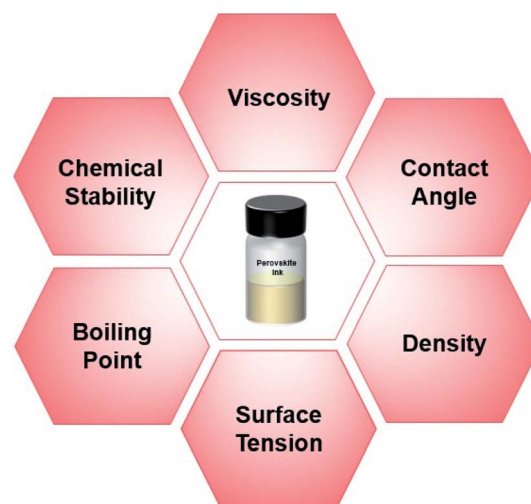


Fig. 5 Key rheological characteristics of high-performance perovskite precursor inks.



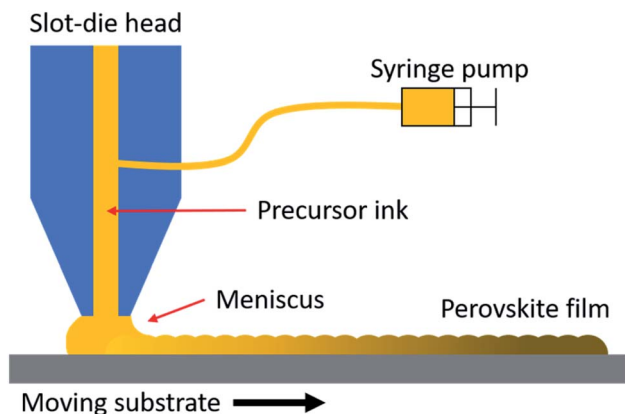


Fig. 6 Schematic illustration of the slot-die coating process.

In contrast, single-step processable inks have also been reported by incorporating starch as a 'rheological modifier',^{126,127} which created a suitable viscosity for the fabricated perovskite inks to be deposited with a suitable thickness without increasing the concentration of perovskite precursors.¹²⁶ Roll-to-roll perovskite-based printed films and flexible solar cells have recently been demonstrated utilizing such inks, reaching a maximum power conversion efficiency close to 10% with required viscosities, with 50% less usage of the raw precursor materials along with a single processing step.¹²⁶

Combined with advancements in similar rheological characteristics research, the rapid technological developments for material deposition schemes have also made it possible to achieve scalable layer formations of active layers for various next generation-based solar cell technologies.^{132–134} This not only enables scalability of the energy systems but also achieves electrical, optical, dielectric, or optoelectronic properties of active layers with a reliable process control.^{135–137}

In this regard, various scalable coating methods for large-area perovskite precursor deposition similar to other next generation-based PV technologies have also been explored to develop large area-based PSC technology on numerous substrates.^{138–140} Some of these established scalable coating methods have been discussed in the following sub-sections.

4.1 Slot-die coating of perovskite precursor inks

Slot-die coating has remained one of the most popular schemes in fabricating flexible organic solar cells, as it allows the possibility for rapid coating and roll-to-roll fabrication of active layers on flexible substrates.^{141–143} In this process, the slot-die head is placed close to the substrate and the ink is pumped into the head using a syringe. This creates a bridge of ink between the head and the substrate, which allows for a clean and rapid deposition of active layers on the desired substrates (Fig. 6).^{141,144}

Vak *et al.* reported one of the first demonstrations of slot-die coating for producing a perovskite light-absorbing layer by modifying a 3D printer with a two-step processing approach.¹⁴⁵ First, the precursor ink of PbI_2 was coated on ZnO and dried to produce a PbI_2 -coated ETL layer. Next, the substrate containing

the active layers was dipped in the MAI solution to obtain the perovskite layer. Finally, the PSC assembly was completed by fabricating a P3HT-based hole transporting layer (HTL) and vacuum evaporating the silver (Ag) contact layer. The fabricated PSC exhibited an efficiency of 11.6%.

As a further advancement, large-area and roll-to-roll fabrication of glass and flexible perovskite solar cells, respectively, in a planar n-i-p configuration was demonstrated with slot-die printed active layers, except for the evaporated metal electrode.⁹⁸ In this work, the perovskite light-absorbing layer was also achieved with a two-step material deposition process, where the PbI_2 ink in DMF solvent was first slot-die coated on a ZnO-based ETL layer with various optimizations using gas quenching treatments. Next, the MAI solution was also coated with the same slot-die coating process to crystallize the perovskite light-absorbing layer. The HTL was achieved by coating with a P3HT solution followed by vacuum evaporation of the Ag contact layer. The fabricated devices on glass showed an efficiency of 11.96% on glass substrates. In contrast to rigid substrates, flexible perovskite solar cell modules were produced with roll-to-roll production on a 10 cm × 10 cm polymer substrate with five serially connected cells.

Demonstrations of single-step slot-die coatings are also reported wherein mixed cations,^{146,147} additives,^{148,149} and compatible solvents have been used to achieve homogeneous and large-area perovskite light-absorbing layers.^{66,141} For example, Schmidt *et al.* reported a single-step slot-die processable coating of perovskite precursor ink that achieved 4.9% conversion efficiency on flexible ITO-PET substrates.¹³⁸ Slot-die coating of a novel precursor ink for triple mesoscopic printable perovskite solar modules was also recently demonstrated; a conversion efficiency of ~13% was obtained over an active area of 60.08 cm² when measured under full sunlight illumination intensity.⁶⁶

These demonstrations suggest that single-step coating processes with slot-die coating might be more suitable for large-scale production of PSC technology. Reaching the desired result is made possible by forming a favorable combination of suitable

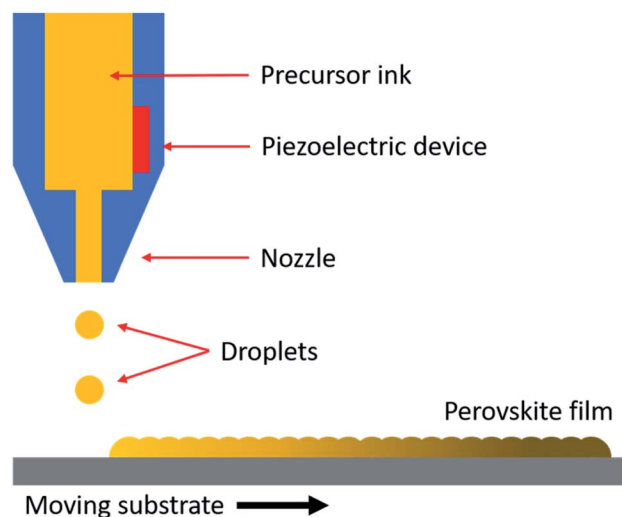


Fig. 7 Schematic illustration of the inkjet printing process.



precursor ink and substrate, along with the improved drying process of the precursor ink and its associated crystal growth.

4.2 Inkjet printing of perovskite precursor inks

The inkjet printing technique offers precise drop on demand (DOD)-based patterning for a variety of materials. In this method, the precursor ink remains stored in a nozzle, and pressure is created through a piezoelectric device to form the droplets. This allows for very precise control over the ink flow, which results in the smooth deposition of active materials over several types of substrates (Fig. 7).¹⁵⁰

The scalability from lab-sized devices to large-area modules can be achieved by the rapid inkjet printing process, where individual layers like in slot-die coating can be printed directly on the desired substrates. Hashmi *et al.* demonstrated inkjet infiltration of a perovskite precursor ink on lab-sized PSCs and highlighted the performance reproducibility and reliable process control among the fabricated individual cells of the triple mesoscopic printable perovskite solar cells.¹⁵ Similarly, Li *et al.* demonstrated inkjet printing of the perovskite precursor in the mesoporous n-i-p device configuration, where the perovskite precursor ink was deposited on TiO₂-based ETLs. The devices showed an efficiency of 12.3% in lab-sized PSC devices when measured under full sunlight intensity.¹⁵¹

Recently, Panasonic Corporation announced 16.09% solar-to-electrical energy conversion for a glass-based large-area perovskite solar module by using a coating method based on inkjet printing. In their module, every individual layer of the device design – including the perovskite layer – was deposited utilizing inkjet printing technology.¹⁵² Another commercial player has also been developing large-area inkjet-printed flexible perovskite solar modules, which have started to become integrated into their commercial products.¹⁵³

4.3 Blade-coating

Blade-coating is another potentially scalable deposition method that is widely used in various demonstrations of fabricating perovskite solar cells.^{154–157} Fig. 8 illustrates the schematic of the

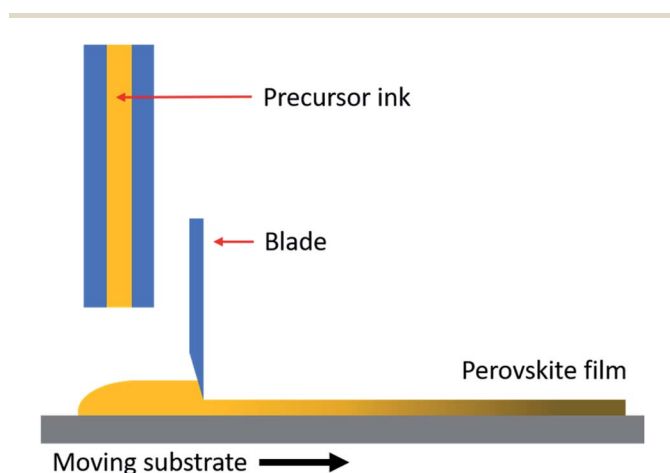


Fig. 8 Schematic illustration of the blade-coating process.

blade-coating process, in which the precursor ink is dropped in front of a metallic or glass blade and then swept forward on a moving substrate to deposit a wet precursor layer.^{158,159} The perovskite film thickness is determined by a few factors, including the meniscus of the solution that forms between the blade and substrate, the speed of the moving blade, the viscosity of the ink, and the concentration of the precursor ink.

Similar to slot-die coating, both single- and two-step processing approaches can be applied to perovskite light-absorbing layer fabrication.^{154,156} Gas and solvent quenching, and heating techniques have also remained popular schemes for controlling the crystallization and drying of the wet layers deposited through blade-coating from their respective precursor inks.^{160,161}

Deng *et al.* performed single-step blade-coating of a perovskite precursor ink on glass substrates, by which 12.8% and 15.1% solar-to-electrical conversion efficiencies were achieved with two different HTM layers.¹³⁹ The fabricated ink was obtained by dissolving MAI and PbI₂ (1 : 1 molar ratio) in DMF, which was then coated with a glass blade on two different HTM (PEDOT : PSS and c-OTPD : TPACA) layers to fabricate and compare the inverted p-i-n configuration. A large grain-sized crystal-based perovskite layer was achieved with the demonstrated blade-coating method, which was effective over a long carrier diffusion length and led to high conversion efficiencies when tested under simulated full sunlight illumination.

In another study, Tang *et al.* applied a novel approach of mixing cesium (Cs⁺) and bromine (Br⁻) ions into the perovskite precursor solution, which also reduced the required film formation temperature.¹³⁵ Pinhole-free perovskite thin films with micrometer-sized grains have been obtained with the assistance of secondary grain growth with methylammonium chloride added into the precursor solution. The fabricated PSCs using such bladed perovskite layer attained an impressive 19.0% solar-to-electrical energy conversion; the best-stabilized conversion efficiency reached 19.3%.¹³⁵ Zhang *et al.* reported an impressive demonstration of an n-i-p design with two-step sequential blade-coating of high-quality perovskite layers for producing efficient solar cells and modules.¹⁶² Their fabrication scheme involved the production of a SnO₂-based compact layer, achieved with a chemical bath process. Next, the sequential blade-coating steps were performed: DMF containing PbI₂-based precursor ink was first bladed over the compact layer and heated to achieve PbI₂ films. Then the mixed solution of FAI, methylammonium bromide (MABr), and methylammonium chloride (MACl) in isopropanol (IPA) was sequentially bladed over the PbI₂ layers, followed by an annealing step at 150 °C for perovskite crystallization. The fabricated solar cells with this two-step blade-coated processing yielded a conversion efficiency as high as >20% among lab-sized solar cells, whereas the large-area (5 cm × 5 cm and 10 cm × 10 cm) modules exhibited 16.54% and 13.32% conversion efficiencies, respectively.

4.4 Spraying

Similar to the previously discussed scalable fabrication schemes, spraying has also been widely used for precursor ink deposition to achieve large-area perovskite layers but also, deposition of other



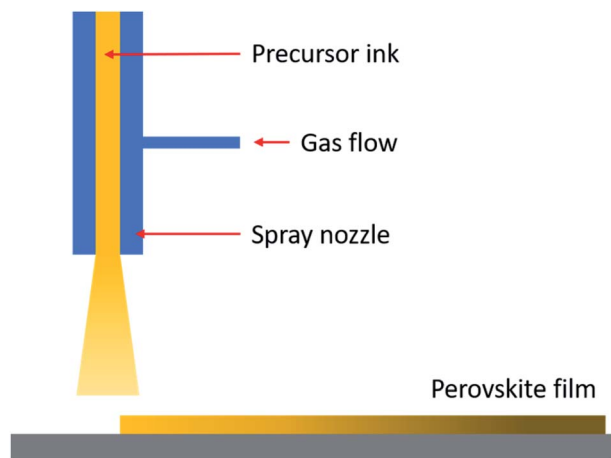


Fig. 9 Schematic illustration of the spraying process.

transporting layers.^{100,163} This solution-based deposition scheme typically utilizes an ultrasonic tip vibrator to create a solvent mist or ink droplets that are directed to the substrate.¹⁶³ To do this, N₂ or O₂ can be used as a carrier gas to produce wet films on the desired substrates (Fig. 9).

Barrows *et al.* coated perovskite layers with a single step by spraying mixed solutions of MAI and PbCl₂ in DMF and DMSO solvents over PEDOT : PSS, and achieved 11% solar-to-electrical conversion efficiency in the inverted p-i-n configuration for lab-sized PSCs.¹⁶⁴

Boopathi *et al.* controlled the volume of MAI through airbrush spraying followed by the deposition of PbI₂ through spin-coating to attain a uniform, stoichiometric and continuous perovskite film.¹⁶⁵ Their experiments showed that either a deficiency or surplus in the volume of MAI generates poor crystallinity and morphology, which gradually reduces device performance.¹⁶⁵ A power conversion efficiency (PCE) of 11.66% was reported when 300 μL of MAI solution was sprayed on 100 nm coated PbI₂ films. With data from 50 devices, the researchers demonstrated 10–11% solar-to-electrical conversion efficiencies under full sunlight illumination testing conditions. The inverted p-i-n device architecture of Ramesh *et al.* achieved an average power conversion efficiency of >9% using a single-step processed lead halide precursor ink that was similarly deposited through the spray-coating technique.¹⁶⁶

From the perspective of scaling up, Tait *et al.* reported a perovskite PV module with a conversion efficiency of 11.7% with a 3.8 cm² aperture area using pinhole-free perovskite layers generated with ultrasonic spray-coating.¹⁶⁷ Similarly, fully spray-coated and scalable PSCs have also been reported with triple cation-based precursor ink formulation. These precursor inks have successfully been sprayed and converted into efficient light-absorbing perovskite layers, along with other sprayed active layers for producing high-performance and large-area PSCs.¹⁶⁸ This also offers the possibility for testing other novel multi-cation-based precursor inks that have been demonstrated for producing high-performance and lab-sized solar cells based on the spin-coating fabrication of perovskite light-absorbing layers.^{169,170}

4.5 Other emerging scalable techniques for perovskite precursor deposition

In addition to the abovementioned scalable coating schemes, other interesting approaches have also been reported to produce both scalable and roll-to-roll coating-based rigid and flexible PSCs and modules. One such pioneer technique is gravure printing of active layers, which allows continuous and precise pattern printing on flexible polymer substrates. Kim and co-workers reported a successful fabrication scheme to produce an SnO₂-based ETL, perovskite layer, and Spiro-OMeTAD or poly(3-hexyl thiophene) (P3HT)-based HTL layers using gravure printing on flexible polymer substrates.¹⁷¹ Interestingly, instead of single-step processing, the perovskite layer was fabricated in two steps. The PbI₂ coating was first performed by formulating a precursor ink in DMSO using a custom-built pilot-scale R2R printing machine. The coated PbI₂ roll was then divided into individual sheets, which were dipped in an MAI bath for perovskite layer formation and annealed at 100 °C for 10 minutes. Conversion efficiency of up to 17.2% was achieved for these flexible PSCs with a gravure printed HTM and thermally evaporated Ag contact electrode, over an active area of 0.052 cm².¹⁷¹

In addition to the gravure printing scheme, Hilt *et al.* recently reported a striking rapid spray plasma processing (RSPP) scheme for large-area perovskite layer deposition.^{137,172} In their preliminary method, a novel perovskite precursor ink was deposited using standard spraying in ambient air using an ultrasonic atomizing nozzle.¹⁷² The coated layer was immediately exposed to atmospheric pressure plasma to achieve rapid perovskite crystallization without post-processing steps. This rapid perovskite active layer formation offers the possibility to realize extremely fast inline production.¹⁷² Rolston *et al.* further developed the technique and demonstrated >15% based perovskite modules at production speeds of >10 m min⁻¹, with perovskite active layer deposition at linear speeds of 12 m min⁻¹.¹³⁷

Overall, the impressive progress in research being made with the abovementioned scalable fabrication processes suggests that a variety of precursor ink processing options are available, not only for perovskite layers but also for depositing other active layers of popular device designs of PSC technology. Results indicate that high performance and rapid production of futuristic perovskite solar modules is within reach, hence there is potential to compete with the existing (and currently dominant) Si-based PV systems. Table 3 summarizes several scalable coating methods for scalable perovskite layer deposition that are currently being used to produce large-area solar modules on a variety of substrates.

5. Evolution of stability of large-area perovskite solar modules with stable perovskite precursor inks

Like other existing next-generation-based photovoltaic technologies, one of the bottlenecks for the awaited commercial success of PSC technology is related to the long-term



Table 3 Recently reported large-area perovskite solar modules were produced by using scalable perovskite precursor inks along with various scalable coating techniques

| Device structure | Perovskite ink composition | Coating method | Active area (cm ²) | PCE (%) | Ref. |
|---|--|----------------|--------------------------------|-----------|------|
| Glass/ITO/PEDOT : PSS/perovskite/C ₆₀ /PC ₆₁ BM | MAI and PbCl ₂ (3 : 1 molar ratio) in DMF | Slot-die | 10 | 8.3 | 146 |
| Glass/FTO/mp-TiO ₂ /ZrO ₂ /carbon/perovskite | MAI and PbI ₂ in GBL with 5-AVAI additive | Slot-die | 60.08 | 12.9 | 66 |
| Glass/ITO/c-TiO ₂ /perovskite/Spiro-OMeTAD | MAI, PbCl ₂ , and Pb (CH ₃ COO)·3H ₂ O in DMF | Slot-die | 168.75 | 11.8 | 173 |
| PET/ITO/SnO ₂ -KOH/perovskite/Spiro-OMeTAD/Au | FAI, MABr, PbI ₂ , and PbBr ₂ in DMF and DMSO | Slot-die | 16.07 | 15 | 116 |
| Glass/FTO/c-TiO ₂ /perovskite/Spiro-OMeTAD | MAI and PbI ₂ in DMF and DMSO | Inkjet | 2 | 17.7 | 39 |
| Glass/FTO/TiO ₂ /perovskite/Spiro-OMeTAD | MAI and PbI ₂ in DMSO : GBL | Inkjet | 4 | 13.2 | 174 |
| Not reported | Not reported | Inkjet | 802 | 16.1 | 152 |
| Glass/FTO/SnO ₂ /perovskite/Spiro-OMeTAD | MAPbI ₃ with PbCl ₂ and Pb(CH ₃ CO ₂) ₂ ·3H ₂ O in DMF | Blade | 16.16 | 11.0 | 175 |
| Glass/ITO/PTAA/perovskite/C ₆₀ /BCP | MAPbI ₃ in DFM mixed with LP in DMF | Blade | 33.0–57.2 | 15.3–14.6 | 29 |
| Glass/FTO/SnO ₂ /perovskite/Spiro-OMeTAD | FAI, MABr, PbI ₂ , and PbBr ₂ in DMF : DMSO (4 : 1 volume ratio) | Blade | 100 | 13.3 | 162 |
| PET/ITO/PEDOT : EVA/perovskite/PCBM : BCP | PbI ₂ , PbBr ₂ , HC(NH ₂) ₂ I and CH ₃ NH ₃ I in DMF : DMSO | Blade | 36 | 17.2 | 176 |
| Willow glass/ITO/PTAA/perovskite/C ₆₀ /BCP/Cu | MAPbI ₃ in 2-ME | Blade | 42.9 | 15.86 | 120 |
| Glass/ITO/TiO ₂ /perovskite/Spiro-OMeTAD | PbCl ₂ : MAI and PbAc ₂ : MAI in DMF | Spraying | 3.8 | 11.7 | 167 |
| Glass/FTO/TiO ₂ /perovskite/PTAA | MAI and PbCl ₂ in IPA | Spraying | 40 | 15.5 | 100 |
| Glass/FTO/c-TiO ₂ /mTiO ₂ + G/perovskite/Spiro-OMeTAD | FAI, PbI ₂ , MABr, PbBr ₂ , and CsI in DMF/DMSO | Spraying | 108–82 | 13.4–15.3 | 140 |
| Glass/ITO/NiO/Cs _{0.17} FA _{0.83} PbI ₃ /C ₆₀ | MAI, CsI and PbI ₂ in DMF : DMSO (1 : 2 volume ratio) | RSPP | 5.9 | 15.2 | 137 |
| Glass/FTO/TiO ₂ /ZrO ₂ /carbon/perovskite | MAI and PbI ₂ in GVL and MeOH | RbM | 220 | 9 | 177 |

photovoltaic performance stability.^{178–180} In this regard, inherent material-based degradation,^{118,181} composition of precursor inks, effective perovskite layer crystallization, unique device designs, and effective sealing strategies significantly influence the overall stability of the fabricated PSCs and large-area modules against simulated and natural climatic conditions.^{12,182}

Bu *et al.* used a scalable mixed cation ink of perovskite precursor to produce a large-area flexible perovskite solar module (PSM), which was deposited on an Alfa-SnO₂ compact layer-based flexible PET polymer foil *via* the spin-coating technique.¹⁸³ This scalable ink was formulated by dissolving 1.3 M organic cations (0.85 FAI and 0.15 MABr) and 1.4 M mixed lead salts (0.85 PbI₂ and 0.15 PbBr₂) in a solvent of DMF/DMSO (4 : 1, by volume). Next, 34 μL of CsI solution (pre-dissolved as a 2 M stock solution in DMSO) was added to achieve the desired Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})₃ perovskite precursor solution. The flexible large-area (5 cm × 6 cm) module exhibited impressive (>15%) solar-to-electrical conversion efficiency over an active area of 16.07 cm² when measured under full sunlight intensity conditions. Moreover, the fabricated flexible module also retained 80% of its original efficiency without encapsulation after 1000 h in dark storage combined with ambient air at ~20% relative humidity (RH) conditions.¹⁸³

Nia and co-workers recently demonstrated >17% solar-to-electrical conversion energy based on a large-area PSM on a glass substrate with an active area of 42.8 cm².¹⁸⁴ The perovskite precursor ink to be coated on the large area was prepared by mixing FAPbI₃ (1.47 M) and MAPbBr₃ (0.18 M) complexes in 1 mL of mixed DMF/DMSO solvent. Next, 0.05 M CsI solution

was added to the mixed solution to complete the recipe, in which the stock solution of CsI was made by dissolving 389.71 mg of CsI powder in 1 mL DMSO. The fabricated ink was deposited on a TiO₂-based ETL to produce a PSM with an n-i-p configuration. In combination with a poly(triarylamine) (PTAA)-based HTL, the fabricated modules showed not only higher solar-to-electrical energy conversion efficiency, but also exhibited impressive stability *via* maintaining >90% of the initial efficiency after 800 h of thermal stress at 85 °C.

In addition to the large-area modules based on conventional n-i-p and p-i-n configurations, other configurations such as the hole conductor-free carbon-based triple mesoscopic printable perovskite solar cells (CPSCs)^{185,186} have also been recognized as potential low-cost configurations, with a proven record of exhibiting high stability when tested under various natural and simulated environmental conditions.^{12,187} The promising demonstrations of scalability and stability reported with this unique device design can be explained by several factors such as (1) the hydrophobic nature of the carbon electrode, which effectively suppresses moisture penetration in the device structure,¹⁸ (2) effective sealing procedures for retarding the rate of degradation,^{12,187} and (3) the novel perovskite precursor ink, which has been introduced with scalable fabrication schemes such as inkjet printing^{15,188} or slot-die coating⁶⁶ methods. As a result, this low-cost device design of the PSC ensures scalability with reliable process control for the successful deployment of this low-cost PV technology.^{15,189}

In addition to research labs, several companies have also recently built or announced the production of large-area perovskite modules.^{190–192} This indicates the relevance and



Table 4 Recently reported stable large-area perovskite solar modules with scalable precursor ink compositions of perovskite light harvesters

| Device structure | Perovskite precursor ink | Method of deposition | Active area (cm ²) | Efficiency (%) | Stability | Ref. |
|---|--|----------------------|--------------------------------|----------------|---|------|
| Glass/FTO/SnO ₂ /carbon/perovskite/PEABr/PMMA/Spiro-MeOTAD/Au | The perovskite solution of Cs _{0.05} FA _{0.8} MA _{0.15} PbI _{2.5} Br _{0.5} for the conventional planar structure was obtained by dissolving CsI, FAI, MAI, PbI ₂ , and PbBr ₂ in DMF and DMSO and stirring the solution at 60 °C for 3 h. The DMSO/DMF ratio was 1 : 4 | Drop-casting | 4.32 | 8.7 | Retains more than 92% of its initial performance after 3000 h of damp-heat aging at 85 °C/85% relative humidity | 195 |
| Glass/FTO/ETL/perovskite/[M ₄ N]BF ₄ /HTL/Au | The FA _{0.91} Cs _{0.09} PbI ₃ perovskite precursor ink was prepared in mixed solvents (DMF : DMSO = 4.75 : 1) with a concentration of 1.25 M, 23 mol% MACl was added | Slot-die coating | 7.92 | 19.6 | Maintained over 80% of its initial efficiency after 551 h at 25 °C, humidity < 20% | 41 |
| Glass/FTO/TiO ₂ /perovskite/Spiro-OMeTAD | FAI (1 M), PbI ₂ (1.1 M), MABr (0.2 M), PbBr ₂ (0.22 M) and CsI (0.05 M) in DMSO and DMF (1 : 4 v/v) | Spin-coating | 8.1 | 12.7 | Retains 85% of its initial PCE after 400 h with an AM 1.5G Oriol solar simulator at an illumination intensity of 100 mW cm ⁻² | 196 |
| Glass/FTO/c-TiO ₂ /perovskite/Spiro-OMeTAD/Ag | A 30 wt% and 45 wt% equimolar ratio MAI and PbI ₂ precursors with different amounts of MACl additive (15%, 30%, 50%, 70%, and 100% molar ratios) in a mixed solvent (NMP/DMF 9/8 volume ratio) were used. The typical recipe for 45 wt% precursor with 30% MACl additive is 0.2 g MAI, 0.580 g PbI ₂ , 0.025 g MACl, 0.524 g NMP and 0.429 g DMF | Blade-coating | 11.09 | 17.33 ± 0.28 | Retains 80% of its initial efficiency after 3000 h measured in air at AM 1.5G and illumination at 100 mW cm ⁻² | 197 |
| Glass/FTO/bi-TiO ₂ /n-TiO ₂ /perovskite/Spiro-OMeTAD/Au | (HC(NH ₂) ₂ PbI ₃) _{0.85} (CH ₃ NH ₃ PbBr ₃) _{0.15} prepared from mixing HC(NH ₂) ₂ PbI ₃ and CH ₃ NH ₃ Br ₃ in DMF and DMSO with the corresponding volume ratio | Spin-coating | 16 | 12.1 | Remains stable after 2 months of storage under ambient conditions | 198 |
| PET/ITO/SnO ₂ /perovskite/SpiroOMeTAD/Au | 1.3 M organic cations (0.85 FAI and 0.15 MABr) and 1.4 M mixture of metal lead salts (0.85 PbI ₂ and 0.15 PbBr ₂) in a mixture solvent of DMF/DMSO (4 : 1, by volume), and then a 34 μL CsI solution (pre-dissolved as a 2 M stock solution in DMSO) was added to achieve the desired | Slot-die coating | 16.07 | 14.47 | Retains 80% of its initial efficiency after 1000 h dark storage in ambient air (~20% RH) without encapsulation | 183 |
| Glass/ITO/PEDOT : PSS/MAPbI ₃ /C ₆₀ /BCP/Ag | Cs _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ perovskite precursor solution with excess lead halide An equal amount of MAI and PbI ₂ was dissolved in 2P to make a precursor solution with a concentration of 1.5 M | Spin-coating | 25.2 | 14.36 | 63% of the efficiency was left when the cell was exposed to air with a relative humidity of 30–50% for 1 month | 199 |
| Glass/FTO/c-TiO ₂ /m-TiO ₂ /perovskite/Spiro-MeOTAD/Au | H ₃ NH ₃ I · 3CH ₃ NH ₂ and PbI ₂ · CH ₃ NH ₂ , in a molar ratio of 1 : 1; CH ₃ NH ₃ I · 3CH ₃ NH ₂ | Spin-coating | 27.5 | 12.1 | Maintained over 90% of its initial efficiency after 500 h; pressure, temperature, and peeling speed were 120 bar (thickness of 400 nm), 50 °C, and 50 mm s ⁻¹ respectively | 200 |
| Glass/ITO/PTAA/perovskite/C ₆₀ /BCP/Cu | 1 M MAPbI ₃ in DMF | Blade-coating | 30.82 | 15.3 | PCE is maintained over 20 days of storage in the dark in a N ₂ atmosphere | 201 |



Table 4 (Contd.)

| Device structure | Perovskite precursor ink | Method of deposition | Active area (cm ²) | Efficiency (%) | Stability | Ref. |
|---|--|-----------------------------|--------------------------------|-----------------------|--|------|
| Glass/FTO/c-TiO ₂ /m-TiO ₂ /perovskite/Spiro-OMeTAD/Au | CH ₃ NH ₃ I·3CH ₃ NH ₂ and PbI ₂ ·CH ₃ NH ₂ , in a molar ratio of 1 : 1 | Pressure processing | 36 | 15.7 (12.1 certified) | Kept 90% of its initial efficiency after continuous working at the maximum power point under light for 500 h | 200 |
| Glass/FTO/SnO ₂ /perovskite/Spiro-MeOTAD/Au | The CsBr film deposition rate was maintained at 0.3 Å s ⁻¹ . After the crucible cooled down, the PbI ₂ films were deposited successively at a rate of 3 Å s ⁻¹ . Then, the as-prepared composite films were transferred into a tube furnace facing another glass substrate with FAI/FACI film sprayed on it | Spin-coating | 41.25 | 17.29 | Maintained 83% of its initial efficiency after 200 h under ambient conditions (RH = ~30%, 25 °C) | 50 |
| Glass/FTO/cTiO ₂ /mTiO ₂ /perovskite/Spiro-OMeTAD/Au | PbI ₂ substrates and MAI in IPA solution (10 mg mL ⁻¹) | Vapor-solid reaction method | 50.6 | 12.6 | Retaining ~91% of the initial PCE value after 1630 h of an endurance test under dark and dry conditions (relative humidity < 30%) | 140 |
| Glass/FTO/TiO ₂ /ZrO ₂ /carbon/perovskite (drop cast perovskite through the carbon layer) | PbI ₂ and CH ₃ NH ₃ I, in a molar ratio of 1 : 1, in γ -butyrolactone | Blade-coating | 70 | 10.74 | Maintained over 95% of its initial efficiency after 2000 h under ambient conditions (temperature \approx 25 °C, and humidity \approx 65% RH) | 99 |
| Glass/ITO/SnO ₂ /perovskite/Spiro-OMeTAD/Au | A mixed organic cation solution (FAI 592 mg, MAI 296 mg, MABr 74 mg, MACl 74 mg, dissolved in 10 mL isopropanol) was spin-coated at 3000 rpm for 30 s | Spin-coating | 91.8 | 10.25 | Kept 90% of the initial efficiency for more than 450 h | 108 |
| Glass/FTO/cTiO ₂ /mTiO ₂ /mZrO ₂ /m-carbon/perovskite | An equimolar solution of PbI ₂ and MAI in γ -butyrolactone | Screen-printing | 198 | 3–5 | Maintained its performance for over 288 h at 70% RH. It was then stored in a box with silica (\approx 30% RH) and tested infrequently. After 528 h following fabrication, it had reached almost 5% PCE, 19.6 V V _{oc} (0.891 V per cell), 125 mA J _{sc} (13.9 mA cm ⁻²), and 40% FF | 202 |
| Glass/FTO/TiO ₂ perovskite/NBP/MoO ₃ /Au | — | Vacuum deposition | 400 | 21.3 | The efficiency increased by 1% from the original value in the air at a humidity of 35% for 189 days | 203 |



importance of producing efficient and large-area PSMs on a variety of substrates through intelligent designing of novel configurations,^{191,192} along with the development of novel and scalable precursor inks^{193,194} that can contribute to the continuous improvements in solar-to-electrical energy conversion and show impressive stability when tested under harsh environmental conditions. Table 4 summarizes the descriptions of large-area stable PSMs reported in recent years with various scalable perovskite precursor ink formulations.

6. Summary and conclusions

The emergence of solution-processed perovskite light harvester-based photovoltaic technology has shown potential for efficient and bulk electricity generation, which may aid in the response to the growing global energy demand. The versatility and use of low-cost, easily available materials offer great flexibility in designing a wide variety of configurations that can be fabricated on numerous substrates, such as flexible polymers or rigid glass, according to the targeted applications.

The intense research and development activities that have progressed in recent years have provided the necessary understanding for transforming these materials into solution-processable inks or paste that can produce this technology with established and scalable coating or printing methods, which may impact production costs. In addition, these scalable production schemes also provide opportunities to scale up technology on both rigid and flexible substrates with a reliable process control that significantly influences the commercial success of nanotechnology-based electronics or advanced energy systems.

Overall, fabricating novel and advanced perovskite precursor inks to support the scaling up of PSC technology has remained one of the key focus areas in the past decade, due to the potential to achieve efficient, scalable, and stable device configurations of this solution-processed and low-cost PV technology. Fabricating such advanced precursor inks with tunable characteristics consequently provides notable flexibility for the various established and scalable coating methods discussed in this review.

Interestingly, although advanced research trends have emerged for examining key rheological characteristics, which led to developing a variety of scalable perovskite precursor inks, their deposition through blade coating or slot die coating schemes appear to be the most predominant method for producing scalable PSCs.^{162,173,201,204} This is understandable, since the post-processing methods such as selective laser scribing, followed by large-area coatings of active layers including the perovskite-based light absorbing layer by these schemes have been proposed to facilitate the production of established serially connected modules.^{205–207}

In contrast, other potential scalable methods such as drop-on-demand inkjet printing^{136,208–210} have yet to be proven as a reliable process step for large perovskite layer deposition in order to overcome advanced key challenges related to creating flexibility in pattern designs of any choice through high precision and resolution.^{15,17,211} These challenges call for the

development of room temperature-based chemically stable precursor inks that can pass through without clotting the micro-nozzles of the inkjet cartridges, in order to deliver precise microlitre-sized drop volumes over the desired surfaces.^{15,17}

In this regard, some interesting guidelines may be taken from a few novel additives^{126,127} discussed earlier in this work for developing desired stable perovskite precursor inks to be used with inkjet printing technology. These additives were claimed to influence the chemical stability of the formulated inks when used with blade coating or gravure printing-based material deposition methods. Thus, use of such novel additives might also aid in developing chemically stable perovskite ink formulations to be used in inkjet technology for achieving high resolutions based on versatile pattern designs.

Alternatively, other grand challenges such as the development of eco-friendly perovskite precursor inks have also been realized to promote the global green energy transition, which presently is bottlenecked when using classical Pb-based precursor inks. Therefore, interesting progress in this growing area of ecologically friendly precursor ink development may also be anticipated, which could provide new opportunities for the safe integration of this low-cost and efficient PV technology.

Author contributions

Ethan Berger, Mohammad Bagheri, Somayeh Asgari, Jin Zhou, Mikko Kokkonen and Parisa Talebi contributed to manuscript planning and communication, compiling sections with writing, drafting figures and tables, reference management and commenting on the final version of the manuscript. Jingshan Luo, Ana Flávia Nogueira and Trystan Watson contributed with an overview and comments on the manuscript. Syed Ghufan Hashmi supervised the research work and contributed with funding acquisition, outline drafting, reviewing, and editing the text, tables, and illustrations of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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