

Perovskite Patterning via Printed Molecular Templates Towards Scalable Semi-Transparent Solar Cells

Amit Kessel¹, Josh Moon¹, Juan F Benitez Rodriguez¹ Hao Deng^{1,2} and Jacek Jasieniak¹

¹ *Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia.*

² *Department of Mechanical and Aerospace Engineering, Monash University, Clayton, Victoria 3800, Australia.*

jacek.jasieniak@monash.edu

Metal halide perovskites have been the epicentre of research towards high-efficiency, low-cost, printable solar cells. More specifically, semi-transparent perovskite solar cells (ST-PSC) have drawn great interest for applications in building integrated photovoltaics (BIPV) such as solar windows^{1,2}. Conventionally, ST-PSC are realised by thinning the perovskite absorber layer to allow partial light transmission, while also replacing the opaque back electrode with a transparent one. This approach has been shown to produce efficient and stable cells, with window-grade levels of transparency (>30%)³. However, their main drawback is the unavoidable perceived colour (typically red to yellow) due the optical bandgap laying within the visible range, which lowers the colour-rendering index (CRI) and therefore impedes their application in BIPV.

A possible path to overcome this hurdle is by patterning the solar cell in a way that selected regions are entirely transmissive while the others remain fully absorbing. Successfully patterning perovskite films has been an ongoing challenge, mostly due to their sensitivity to common lithographic techniques which can cause the degradation of the film. Yet such device configurations were recently reported by utilising a pre-patterned template, which is removed after the perovskite deposition⁴ and in another study via laser scribing the complete solar cell⁵. While it demonstrated high power conversion efficiencies for a given transparency value (which inherently follow an inverse relationship) along with colour neutrality, the complexity of the processes may hinder its applicability for manufacturing larger than lab-scale devices. An alternative approach has shown that by forming a patterned organosilane hydrophobic template on the substrate through photolithography, the then deposited perovskite solution is naturally repelled from crystallising in those regions and self-assemble into a desired structure⁶. This selective-wetting approach has been since overlooked, owing to the complexity of preparing the patterned hydrophobic template.

Herein, we present a fully scalable technique to prepare self-assembled patterned perovskite films by micro-contact printing a hydrophobic molecular layer of octadecyl phosphonic acid (ODPA) over an ITO substrate prior to perovskite deposition. The proposed parallel patterning method allows for a rapid transfer, regardless of the area and thus minimises interference in the solar cell fabrication process. The effect of the perovskite precursor concentration on the pattern yield is demonstrated, along with characterisation of the induced transparency.

For this purpose, ODPA was utilised due its compatibility with micro-contact printing⁷, stable bond with metal oxide surfaces and the long alkyl chain which entails it with low surface energy⁸.

The patterning process is illustrated in **figure 1** and is comprised from the following steps:

1. An elastomeric stamp is inked by dipping in ODPA solution and then dried with a N₂ gun.
2. The ITO substrate is treated with UV-ozone to form hydroxyl groups on the surface and immediately brought into brief conformal contact with the inked stamp to transfer the molecular template.
3. FACsPbI₃ perovskite solution is spin coated and dewets from the ODPA covered regions.
4. final solvent removal and crystallisation via annealing of the patterned film.

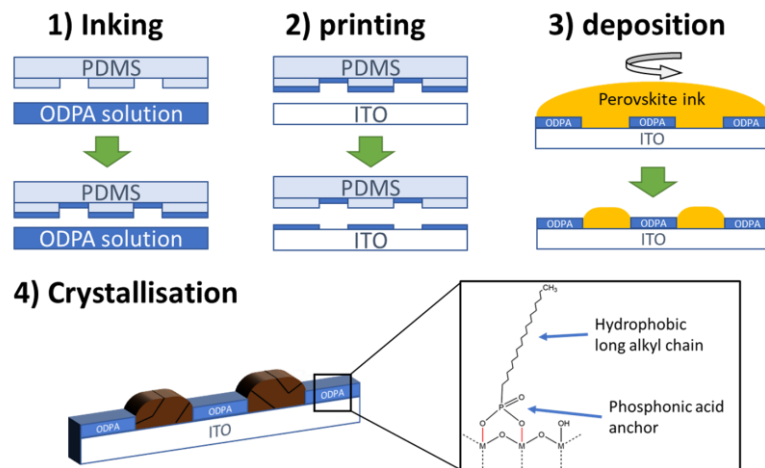


Figure 1. Schematic illustration of the patterning process

First, we confirm the transfer of ODPA onto the ITO and the functionalization of the surface. For that purpose, a PDMS stamp with a periodic array of squares was utilised (**figure 1a**). Due to the ultra-low thickness of the printed ODPA layer, it is not sufficiently visible through an optical microscope nor distinguishable by atomic force microscopy. However, due to the molecule's charge trapping nature⁹, it can be easily imaged through scanning electron microscopy (SEM). **Figure 1b** shows an SEM image of the printed ODPA array, exhibiting a perfect replication of the stamp pattern.

To validate the induced hydrophobicity and characterise the changes in surface energy we conducted sessile drop contact angle measurement for both water and the less polar solvent dimethylformamide (DMF), which is used to dissolve the perovskite precursor (**Figure 2c**). When comparing between bare ITO (treated with UV ozone) and a uniformly covered ODPA surface (printed with a flat stamp), the contact angle rises from 19.1° to 105.5° and 0° to 62.5° for water and DMF respectively, thereby proving the relative hydrophobicity of the printed ODPA layer. For a patterned surface, we observe an intermediate meta-stable state that corresponds to the ratio of the hydrophilic/hydrophobic regions.

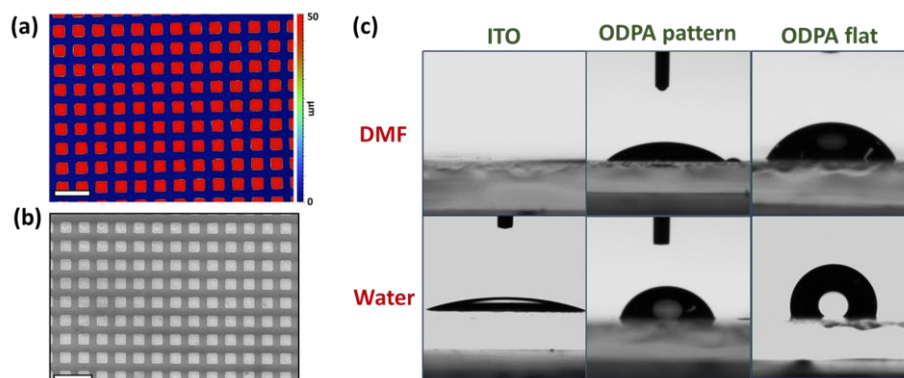


Figure 2. (a) Height profile of the stamp and (b) the corresponding SEM image of the transferred ODPA layer. (c) Contact angle measurement confirming the induces hydrophobicity of the ODPA layer as opposed to bare ITO.

The perovskite solution concentration plays a key role in controlling the rheological properties, including viscosity and surface tension¹⁰, which affects the dewetting dynamics. When varying the concentration range between 0.42-1.67 molar (which corresponds to a plain film thickness between 75-650 nm, with the upper value being typical for maximal light absorption), the wetting dynamics and pattern yield vary substantially along this range (**figure 3a**). Under high concentration, regions with excess solution (owing to the inhomogeneity of the spin coating process) may remain covered, due to an accelerated nucleation¹¹ along with the effect of contact line pinning¹². This can be overcome by reducing the concentration and as a result the intermolecular attraction, which hinders a complete spread prior to nucleation and crystallisation. A deeper examination of the surface morphology (**figure 3b**), shows a gradual increase in thickness from the boundary towards the bulk, which is important to achieve a uniform coating of the remaining layers in a device stack. In addition, SEM imaging reveals densely packed grains (**figure 3c**), indicating an efficient charge transport capability.

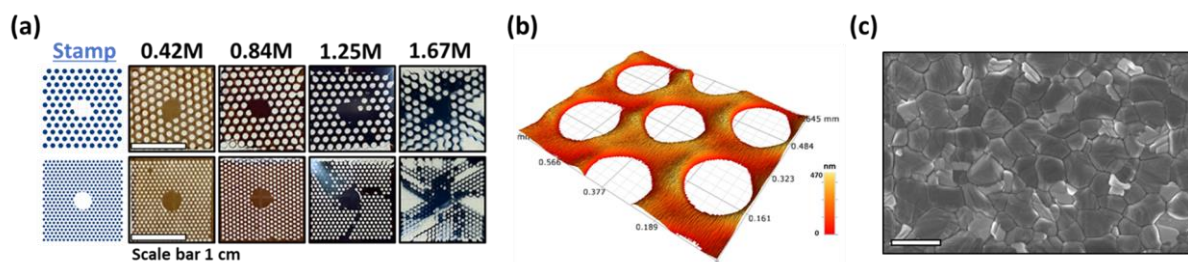


Figure 3. (a) Effect of perovskite solution concentration on the pattern yield. (b) Surface morphology of a representative unit cell. (c) SEM image of the patterned film crystallisation.

Controlling the level of transparency can be readily done by adjusting the amount of exposed area. Compared to a non-patterned plain film, the increase in average visible transmittance (AVT) is proportional to the fraction of exposed area (**Figure 4a,b**). We observe a larger rise in transmittance for the fully-absorbed shorter wavelengths (<550 nm), as opposed to the lower energy photons which are inherently partly transmitted due both lower absorption coefficient and the film's thickness. This results in a flattening of the spectral shape which shifts the perceived colour into a natural appearance (**Figure 4c**). The scalability of this method is further established by fabricating patterned perovskite films over a 25 cm² area, without necessitating any process modifications or additional time (**Figure 4e**).

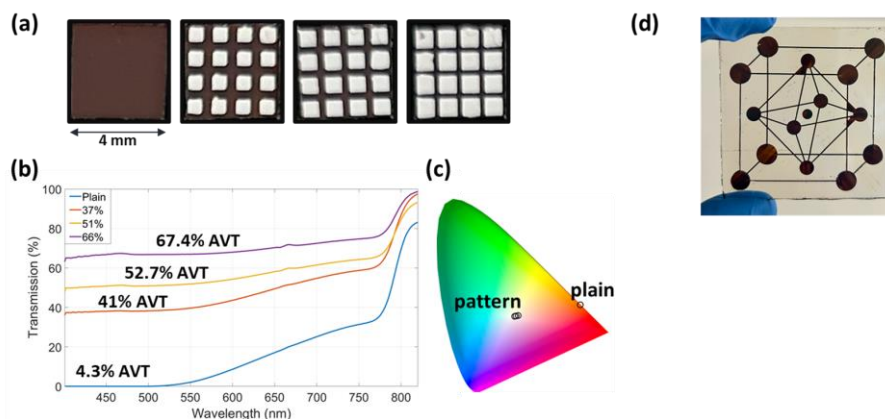


Figure 4. (a) perovskite films with varying % of exposed area and their (b) corresponding transmission spectra, average visible transmittance (AVT) and (c) CIE colour coordinates. (d) large area patterning over 25 cm² substrate.

In summary, we present a low-cost and efficient method for patterning metal-halide perovskites via printing a hydrophobic template on the substrate, that allows for the formation of self-assembled patterned perovskite films. The main benefit of this approach is that a single stamp can generate countless of patterned films without the need for post-processing, thus minimizing the required lithographic steps, and the burden they pose. This simplification of the process offers a seamless pathway for integration into the fabrication line, and can accelerate the implementation of semi-transparent solar cells and other optoelectronic devices such as photodetectors and high-resolution displays.

References

1. Koh, T. M. *et al.* Halide Perovskite Solar Cells for Building Integrated Photovoltaics: Transforming Building Façades into Power Generators. *Advanced Materials* vol. 34 Preprint at <https://doi.org/10.1002/adma.202104661> (2022).
2. Bing, J. *et al.* Perovskite solar cells for building integrated photovoltaics—glazing applications. *Joule* **6**, 1446–1474 (2022).
3. Yu, J. C. *et al.* High-Performance and Stable Semi-Transparent Perovskite Solar Cells through Composition Engineering. *Advanced Science* 2201487 (2022) doi:10.1002/advs.202201487.
4. Lee, W. *et al.* Perovskite microcells fabricated using swelling-induced crack propagation for colored solar windows. *Nat Commun* **13**, 1946 (2022).
5. Ritzer, D. B. *et al.* Translucent perovskite photovoltaics for building integration. *Energy Environ Sci* **16**, 2212–2225 (2023).
6. Lee, W. *et al.* High-Resolution Spin-on-Patterning of Perovskite Thin Films for a Multiplexed Image Sensor Array. *Advanced Materials* **29**, (2017).
7. Breen, T. L., Fryer, P. M., Nunes, R. W. & Rothwell, M. E. Patterning indium tin oxide and indium zinc oxide using microcontact printing and wet etching. *Langmuir* **18**, 194–197 (2002).
8. Guerrero, G., Alauzun, J. G., Granier, M., Laurencin, D. & Mutin, P. H. Phosphonate coupling molecules for the control of surface/interface properties and the synthesis of nanomaterials. *Dalton Transactions* **42**, 12569–12585 (2013).
9. Rampulla, D. M., Wroge, C. M., Hanson, E. L. & Kushmerick, J. G. Charge transport across phosphonate monolayers on indium tin oxide. *Journal of Physical Chemistry C* **114**, 20852–20855 (2010).
10. Habibi, M., Rahimzadeh, A., Bennouna, I. & Eslamian, M. Defect-Free Large-Area (25 cm²) Light Absorbing Perovskite Thin Films Made by Spray Coating. *Coatings* **7**, 42 (2017).
11. McMeekin, D. P. *et al.* Crystallization Kinetics and Morphology Control of Formamidinium–Cesium Mixed-Cation Lead Mixed-Halide Perovskite via Tunability of the Colloidal Precursor Solution. *Advanced Materials* **29**, 1607039 (2017).
12. Mazloomi Moqaddam, A., Derome, D. & Carmeliet, J. Dynamics of Contact Line Pinning and Depinning of Droplets Evaporating on Microribs. *Langmuir* **34**, 5635–5645 (2018).