

Low-temperature and ambient processable all-inorganic CsPbI₃ solar cells

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Hybrid organic-inorganic perovskite materials have garnered significant attention due to their unique ability to adjust their optical and electrical properties through compositional and structural tuning [1-2]. In particular, these defect-tolerant materials can be modified to alter their bandgap, conduction and valence band energy levels, and absorption coefficient, allowing for a wide range of potential applications [3-4]. The exceptional features of hybrid perovskites are contributed by the blend of organic and inorganic elements. One potential setback, however, is the long-term operational stability, which may be limited by the volatility of organic components, among other factors [1-5]. An all-inorganic lead-halide perovskite achieved by replacing the organic cations with alkaline earth metal cations, such as Cs⁺ or in combination with Rb⁺, has garnered significant attention due to its potential to alleviate the stability of perovskite solar cells. These cesium-based inorganic lead halide perovskites have optoelectronic properties that are comparable to those of hybrid organic-inorganic perovskites [6-8]. In addition, these perovskites are characterised by high carrier diffusion distances, low excitonic binding energies, and high photoluminescence quantum yields [7]. Over the years, a diverse selection of inorganic perovskites, both lead-based and lead-free, have been extensively studied and have shown great potential [6,8].

A critical challenge in the path for further developing inorganic perovskite, specifically, CsPbI₃ perovskite formulation, is that higher phase-transformation temperatures (>320 °C) and prolonged sintering are required during processing to obtain photoactive cubic black α -phase [9-12]. Additionally, most literature reports use an inert environment to fabricate inorganic perovskite solar cells. Such a high temperature makes inorganic perovskite incompatible for fabrication on low-cost, flexible substrates such as polyethylene terephthalate (PET) and polyethylene naphthenate (PEN), which are ideal for low-cost and high-throughput manufacturing via roll-to-roll processes. Additionally, maintaining an inert environment is neither economically nor technically feasible in a large-scale R2R manufacturing scenario. Thus, the aim of this study was to develop an ambient-compatible processing method for the fabrication of CsPbI₃ whilst also reducing thermal treatment steps to below the thermal tolerance threshold of PEN substrates, i.e., 180 °C.

To accomplish this, the present work developed a gas-assisted hot-casting method to promote perovskite nucleation and crystallisation, which enabled high-quality CsPbI₃ perovskite films using spin-coating under ambient laboratory conditions (30-50% relative humidity and 20-25 °C). The addition of alkyl ammonium chloride (RACl) along with dimethylammonium iodide (DMAI) to the perovskite formulation reduced the temperature required for the formation of the desired perovskite α -phase to less than 160 °C. The introduction of dimethylammonium iodide (DMAI) in the solution has been found to reduce the phase-transformation temperature of the inorganic perovskite layer [6, 7], but using it alone was found to yield non-uniform films and result in less environmentally stable PSCs under an ambient environment (20-50% RH). The best-performing perovskite solar cells in this work were obtained by alkylammonium chloride (RACl) for surface treatment and alkylammonium iodide as a passivation layer to the precursor formulation, which improved the ambient-processability and stability of the devices.

A fully cubic perovskite phase was obtained through careful control of the film fabrication process. Figure 1a shows some processing methods utilised in incorporating RACl and the XRD characteristics of the resulting films, which showed the optimal film was composed of cubic phase

CsPbI₃. The optimal experimental condition enabled a uniform and dense structure composed of compact grains, as evident in the SEM image presented in Figure 1b, which is comparable to those achieved through more complex crystallisation fabrication techniques on glass-based substrates fabricated under an inert environment.

The optoelectronic characteristics of films containing inorganic perovskite layers were analysed in this study. The films were coated with or without 30mM RACl additive in the precursor formulation and subjected to surface treatment. The results indicated that while the absorption remained constant (Figure 1c), there was a noticeable variation in the PL intensity (Figure 1d). Further characterisation and analyses are underway.

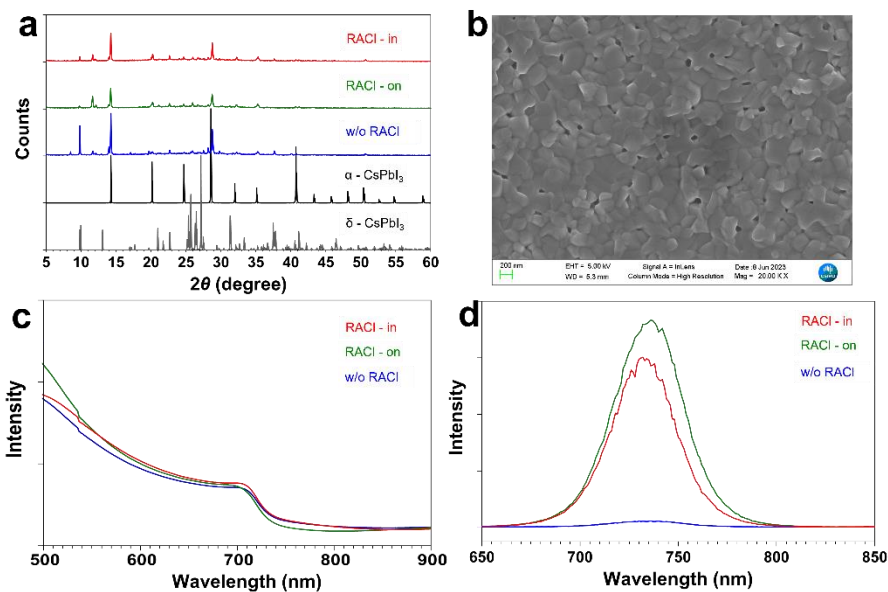


Figure 1. a) XRD patterns of the perovskite films annealed at 160 °C for 3 minutes. c) SEM image of the perovskite film fabricated. c) UV-vis absorption and (d) PL spectra obtained for the fabricated films on ITO under ambient laboratory conditions without humidity control (up to 50% RH).

The optimised films were utilised to fabricate perovskite solar cells in n-i-p configuration with the device structure Glass/ITO/SnO₂/CsPbI₃/Spiro-oMeTAD/Au. All fabrication was carried out under an uncontrolled ambient environment (25 °C, 30-50% relative humidity). The results of the photovoltaic parameters of the devices fabricated using the gas-assisted spin-coating approach are summarised in Figure 2a. The power conversion efficiencies (PCEs) of the devices range between 14-16%, with the highest-performing device exhibiting a PCE of 15.9% at relative humidity of 30 ± 5%. This was achieved through a combination of factors, including a Voc of 1.14 V, Jsc of 19.8 mA cm⁻², and an FF of 71.4%.

When 30mM RACl treatment was applied to a perovskite surface, the resulting device exhibited remarkable PCE stability without any apparent drop (in fact, significant improvement with light soaking) over 20 hours upon MPP tracking under constant 1 sun illumination in an inert environment (Figure 2b) and a decrease of less than 10% over 250 hours of illumination in the ambient environment (RH 15%, 25 °C)(Figure 2c). This starkly contrasted with the perovskite solar cells with perovskite films produced without the RACl additive, which turned yellow and immediately failed. The higher stability of the perovskite solar cells having the gas-assisted hot-casted perovskite film with RACl additive may be related to the decrease in the defect density in

the perovskite film induced by the addition of the RACl. Future characterisation and analyses are underway.

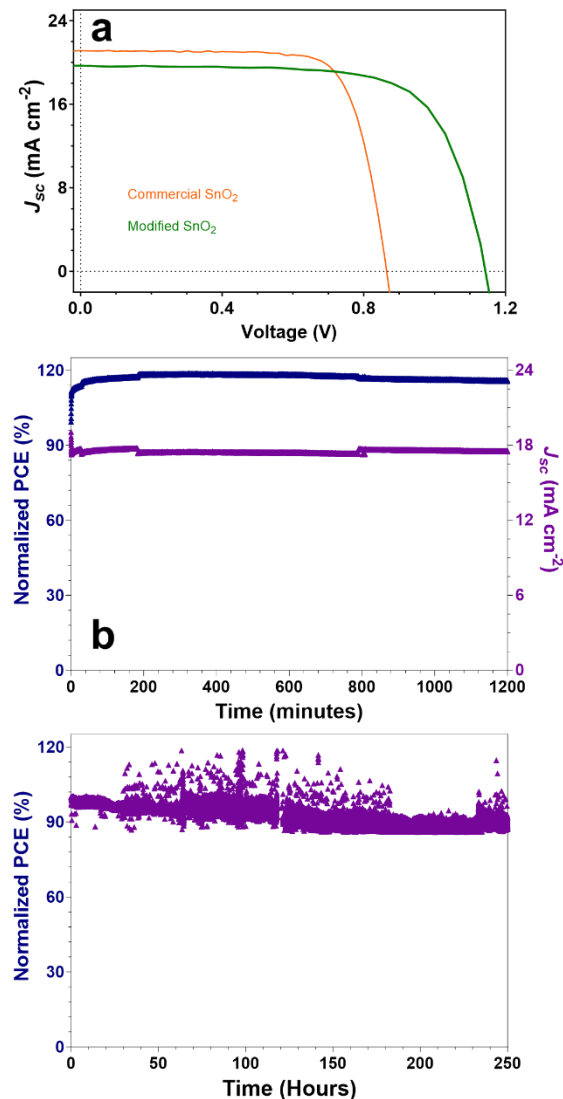


Figure 2. Photovoltaic parameters of PSCs prepared on glass substrates using a coating of perovskite layers with or without 30mM RACl treatment a) J - V curves of the champion device fabricated with 30mM RACl with commercial SnO_2 and home-made SnO_2 nanocrystals. b) MPP of the champion device at 0.84 V for 20 hours under illumination in N_2 without encapsulation. (c) Unencapsulated PSC devices with perovskite layer produced with or without RACl surface treatment were measured at MPP under constant 1-sun illumination for 250 h in ambient air, RH 15%.

It is worth noting that all layers apart from the metal anode were fabricated in low-temperature annealing conditions ($<160^\circ\text{C}$) and ambient laboratory conditions without humidity control (25°C , 30-50% RH). In fact, 160°C annealing temperature was found to be optimal for the fabrication process developed (Figure 3a-d). These conditions favour industrial-scale production, making the gas-assisted spin-coating approach a promising method for manufacturing high-performance CsPbI_3 perovskite solar cells.

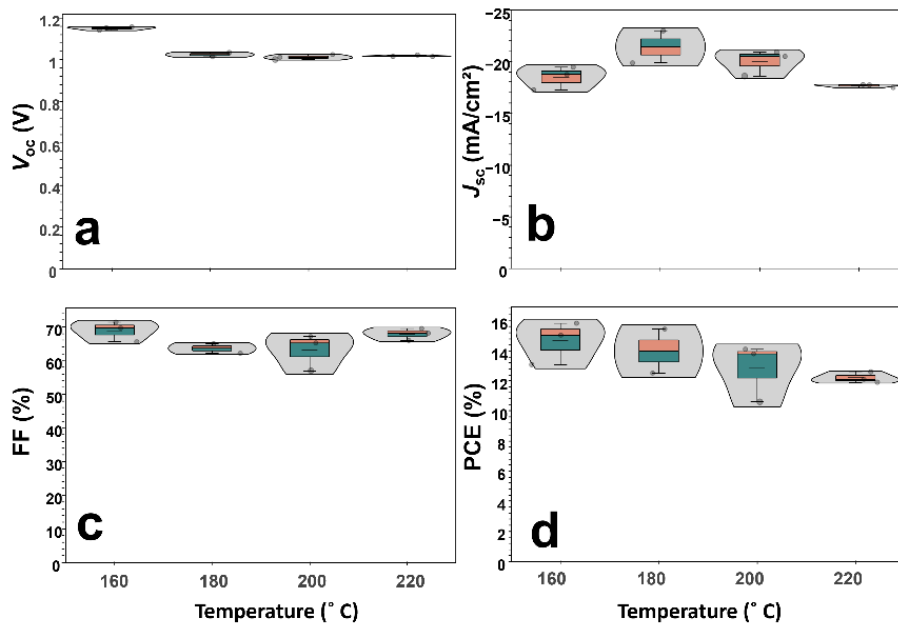


Figure 3. a) PCE, b) FF, c) V_{oc} , and d) J_{sc} distributions for devices fabricated using the gas-assisted under ambient laboratory conditions. The device structure was $\text{ITO}/\text{SnO}_2/\text{CsPbI}_3/\text{Spiro-OMeTAD}/\text{Au}$.

In conclusion, a gas-assisted hot-casting strategy for high-quality CsPbI_3 perovskite films has been demonstrated using low-temperature annealing conditions and fabrication compatibility under ambient room environments. The inclusion of RACl and alkylammonium iodide (RAI) in the perovskite crystallisation process also improved the stability of unencapsulated perovskite solar cells, which retained over 90% of their original PCE after 250 h of continuous 1-sun illumination (RH15%). The devices fabrication with n-i-p configuration achieved a power conversion efficiency (PCE) of over 15%. This study addresses several limitations of existing processing of inorganic CsPbI_3 perovskite layers toward R2R compatibility, which is a crucial step towards developing large-scale, high-performance, and stable PSCs.

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