A novel dimethylformamide (DMF) free bar-cast method to deposit organolead perovskite thin films with improved stability†

Eurig W. Jones,a Peter J. Holliman,*a Arthur Connell,b Matthew L. Davies,b Jennifer Baker,b Robert J. Hobbs,a Sanjay Ghosh,a Leo Furnell,a Rosie Anthonya and Cameron Pleydell-Pearceb

We report a solvent-free approach to synthesizing organolead perovskites by using solid state reactions to coat perovskite crystals onto Al₂O₃ or TiO₂ nanoparticles followed by addition of terpineol affording perovskite inks. We have bar cast these inks to produce photoactive perovskite thin films which are significantly more stable to humidity than solution-processed films. This new method also avoids the use of toxic DMF solvent.

Since the initial reports of organolead halide perovskite solar cells,1,2 device efficiencies have risen rapidly towards 20%.3 It has also been demonstrated that such perovskites work efficiently in a variety of PV device architectures4 including planar TiO₂ charge collection layers5 and mesoporous TiO₂ as well as in batteries6 and sensors.6b Electrically-insulating Al₂O₃ scaffolds7 have been reported, demonstrating that the perovskite absorber layer can efficiently sustain charge transport. This is important because key limiting factors for perovskite solar cells are the surface coverage and crystallisation steps which occur at the perovskite–metal oxide interface during device manufacture. As a result, perovskite device manufacturing is the subject of much interest. A current limitation for one-step, solution processed perovskites is infiltration into the mesoporous scaffold, which can be improved by sequential deposition,8 affording superior surface coverage and avoiding the need for a perovskite capping layer. However, concerns remain over the solvents used for solution processed perovskites9 and the stability of the resulting materials to temperature and/or moisture.10,11 As such, recent reports suggest optimum fabrication conditions such as %RH < 1%,10 which complicates scale up.

To date, the choice of perovskite processing solvent has been limited to dimethylformamide (DMF),1 dimethylsulfoxide (DMSO)12 or γ-butyrolactone (GBL)2 given the need to dissolve the PbX₂ precursor (X = Cl, Br, I). By comparison, methyl ammonium halides are readily soluble in most solvents including water. In this paper, we report that a 1 : 1 ratio of PbX₂ and CH₃NH₂X react readily together with quantitative yield in solvent-free, solid state reactions by grinding/milling (ESI,† Fig. S1). We have also studied the addition of metal oxide nanoparticles (Al₂O₃ or TiO₂) as common scaffold materials for perovskite solar cells during or after the solid state perovskite reaction. After perovskite has formed on the metal oxide surface, to produce a printable ink, we have ground the particles in terpineol as a suspending media rather than a solvent. Perovskite crystals have previously been suspended in DMF12 but here terpineol has been chosen because it has low toxicity and is widely used in printing media. It also possesses a high boiling point (219 °C), which is similar to DMSO (189 °C) which has been reported to stabilise solvent-PbI₂ complexes and inhibit PbI₂ crystallization.13 This also avoids the DMF volatilisation (b.p. 153 °C) during spin coating, which increases perovskite crystal dislocations. Higher boiling solvents also encourage slower perovskite crystal growth during annealing. The resultant inks can then be doctor bladed or bar cast. We have studied the influence of metal oxide loading and found that, for Al₂O₃, a loading of >10% Al₂O₃ is required to cast a uniform layer, presumably because Al₂O₃ acts as a plasticizer. This is more than the 5% Al₂O₃ reported by Carnie et al.14 for their DMF/perovskite/Al₂O₃ nanoparticle precursor in their spin coating based study. The difference is that the perovskite particles are pre-formed on the Al₂O₃ particle surfaces in our inks and no DMF is present unlike previous reports of bar-cast perovskites.15 Visual inspection also suggests that the resulting colloidal inks are stable for > 3 months. An additional advantage of developing inks for meso-scopic perovskite solar cells using a passive Al₂O₃ scaffold is their low-temperature processability. Thus, our inks can be deposited under ambient conditions and heated at 110 °C because high temperature processing is not required to ensure inter-particle “necking” to carry electrical charge as is the case for TiO₂ photo-electrodes.16 This is in line with previous reports for Al₂O₃ where heat processing is shown...
to be complete at 150 °C\(^{17}\) and 110 °C.\(^{14}\) The perovskite ink formation is described in eqn (1) and (2).

\[
\text{[PbX}_2 + \text{Al}_2\text{O}_3] + \text{CH}_3\text{NH}_3X \rightarrow \text{[CH}_3\text{NH}_3\text{PbX}_3 : \text{Al}_2\text{O}_3] \quad (1)
\]

\[
\text{[CH}_3\text{NH}_3\text{PbX}_3 : \text{Al}_2\text{O}_3] + \text{terpineol} \rightarrow \text{Perovskite ink} \quad (2)
\]

For film deposition, a compact 80 nm TiO\(_2\) layer (Solaronix BL) was spin coated (3500 rpm, 60 s) onto TEC15 glass (15 Ω sq\(^{-1}\), NSG) and heated (550 °C for 1 h). Perovskite inks were deposited onto these substrates either by spin coating, doctor blading or bar casting to produce films ranging from 400 nm to ca. 10 μm in thickness. In addition, to drastically increasing the atom efficiency of the perovskite manufacturing process, the stoichiometric nature of these solid state reactions is key to improving the compositional control over the materials produced. Thus, in Snaith et al. original report of perovskite devices,\(^{7}\) a 3:1 ratio of CH\(_3\)NH\(_3\)I:PbCl\(_2\) was used along with spin coating to control layer thickness. However, the I : Cl ratio of the resultant CH\(_3\)NH\(_3\)PbI\(_2\)Cl was reported as 2:1. Effectively, this means that an excess of CH\(_3\)NH\(_3\)I is required to convert all the PbCl\(_2\) into perovskite. Whilst CH\(_3\)NH\(_3\)X waste is less of an issue at the laboratory scale, it is not viable for a scaled process because it multiplies raw material costs and environmental impact which has been reported to be greater for CH\(_3\)NH\(_3\)I than for PbX\(_2\).\(^{18}\) By comparison, in the solid state reactions, CH\(_3\)NH\(_3\)X and PbX\(_2\) can be reacted together in the desired ratio and this ratio is carried through into the resulting perovskite material. A further advantage of solid state reactions is much greater control of trace components (e.g. Cl\(^-\)) which is known to be key to device performance.\(^{19}\)

To prepare organolead perovskites on Al\(_2\)O\(_3\), PbX\(_2\) (X = Cl, Br, I) and Al\(_2\)O\(_3\) nanoparticles (mean size 13 nm) are ground together until there is no further colour change. After adding the desired CH\(_3\)NH\(_3\)X to this the mixture is ground together again. Conversion to a perovskite phase varies depending on the halides used. For CH\(_3\)NH\(_3\)PbI\(_3\)Cl\(_x\), an intermediate non-perovskite yellow phase is obtained (Fig. 1b) which only turns black and converts to perovskite after heating at 120 °C for 50 min (i.e. standard solution processing conditions). A similar intermediate perovskite complex, has been previously reported by Wu et al.\(^{13}\) By comparison, the CH\(_3\)NH\(_3\)PbI\(_3\) ink turns black purely by mechanical mixing and before heating at 120 °C (Fig. 1a). We have defined the pre-heated tri-iodide as “semi-perovskite” ink as the XRD data confirm significant amounts of unconverted PbI\(_2\) are still present, which then decrease after heating. Finally, CH\(_3\)NH\(_3\)PbBr\(_3\) turns orange on grinding which fully converts and increases in crystallinity on heating (ESI,\(^\dagger\) Fig. S3). Upon the addition of terpineol, each reaction continues to completion and we believe the terpineol assists in a wet grinding process whereby the size of the PbX\(_2\) and CH\(_3\)NH\(_3\)X crystals are further reduced and these particles are more intimately mixed enabling intercalation of CH\(_3\)NH\(_3\)X into the lead halide lattice to form crystalline perovskite.

Fig. 1 (a) Semi-perovskite, (b) perovskite intermediate and (c) schematic of perovskite device architecture.

Fig. 2 XRD data of CH\(_3\)NH\(_3\)PbI\(_3\) films manufactured by (a) solution processing, (b) solid state reaction using TiO\(_2\) and (c) deposited on glass from a perovskite ink. * (110), (220), † (310) of perovskite phase, × (Al\(_2\)O\(_3\)), ‡ (101) TiO\(_2\) diffraction lines.
X-Ray powder diffraction data show that the solid state reaction between CH₂NH₃I and PbI₂ produces predominantly the CH₃NH₃PbI₃ phase with only low intensity peaks observed for PbI₂ (Fig. 2b). Unconverted PbI₂ has been reported previously in the two-step solution processing method, even when the substrate is heated to 60 °C, to constrain lateral crystal growth.⁵⁰ The PbI₂ peaks observed in our work (ground samples) more closely resemble data observed for samples deposited on optimally pre-heated (50 °C) substrates, which is typically done to assist small particle formation and improve coverage.¹³ After grinding in terpineol (Fig. 2c), the (110) peak for the perovskite phase increases in relative intensity, confirming that the solid state reaction continues on further grinding in the solvent. Data from line broadening suggest that the average crystal/domain size is ca. 100 nm which is similar to that typically observed purely for one-step solution processing methods rather than the larger 500 nm particle sizes observed using the two-step method.¹⁷ In addition for both ground samples, there is less evidence of preferred orientation (Fig. 2b and c) compared to solution deposited material (Fig. 2a). This is to be expected as the solution deposited samples nucleate and grow directly onto a flat substrate which is heated from below making perpendicular crystal growth much more likely. By comparison, the ground samples nucleate and crystallise onto randomly oriented metal oxide particles so the orientation of their crystal growth will also be randomised.

Photoluminescence (PL) of perovskite films is strongly linked to device efficiency²¹ and so PL microscopy and in situ spectroscopy of perovskite:metal oxide films was carried out to evaluate surface coverage and electron shuttling. The data show that films of doctor bladed CH₃NH₃PbI₃₋ₓClₓ, bar cast CH₃NH₃PbI₃₋ₓClₓ and CH₃NH₃PbBr₃ are all emissive, which suggests they should all be photo-active in PV devices (Fig. 3a-c). As expected, the thicker 7 μm doctor bladed CH₃NH₃PbI₃₋ₓClₓ film (Fig. 3a and f) shows PL intensity which is much greater than that of the equivalent 400 nm bar cast film (Fig. 3b and f). Interestingly, the intensity of the doctor bladed film is comparable to the solution processed image (Fig. 3e and f). In terms of coverage, two issues need consideration. Firstly, there is the coverage of the mesoporous Al₂O₃ film on the substrate and secondly there is the coverage of the perovskite layer on the Al₂O₃ surface. For the doctor bladed film, the perovskite coverage on the Al₂O₃ surface appears to be consistent whilst the mesoporous Al₂O₃ film is much less even. However, there do not appear to be any pin holes in this film which would cause short circuiting in PV devices made from this material. By comparison, the coverage of the perovskite on the Al₂O₃ surface in the bar coated film appears less complete although the mesoporous Al₂O₃ film itself still appears to be complete. For the analogous bar coated CH₃NH₃PbBr₃ sample, greater PL intensity is observed than for the CH₃NH₃PbI₃₋ₓClₓ sample although at λ ca. 540 nm reflecting the larger band gap for the tribromide perovskite. Here, the perovskite coverage on Al₂O₃ seems fairly complete although some areas seem brighter than others suggesting variable particle sizes of perovskite crystals have been deposited (Fig. 3c). To further study scaffold coverage, a TiO₂-based CH₃NH₃PbI₃ paste was bar coated onto a glass substrate. The maximum PL intensity for this sample is ca. 600 cps compared to ca. 12 000 cps for the doctor bladed and ca. 6000 cps bar coated CH₃NH₃PbI₃₋ₓClₓ films. Firstly, this suggests that the perovskite films formed can effectively inject into an electrically-conducting scaffold whilst the PL mapping (Fig. 3d) of TiO₂-based perovskite ink shows areas of low PL intensity across the film surface. As the films are not under load, we expect emission to be faster than injection so the low emission for this film may reflect poor coverage or lower stability of the CH₃NH₃PbI₃ on TiO₂. By comparison, the more uniform emission across the perovskite:Al₂O₃ films confirms better coverage and perovskite stability and could also suggest lower losses at grain boundaries or crystal interfaces where emission might be quenched. Ultimately, assuming that more emission relates to more potential charge extraction in a PV device under load and given the need for PV devices to possess lifetimes of many years this suggests Al₂O₃ scaffolds should be preferable to TiO₂. Furthermore, perovskites which have been solution processed onto metal oxide scaffolds exhibit slightly blue-shifted emission (760 nm vs. 750 nm) as a result of confined growth within mesoporous films.²³²² Figure 3f shows that the PL peaks of the ink-based films are similarly blue shifted compared to the solution processed film. This suggests that the perovskite crystals from perovskite inks are similar in size to those grown inside scaffolds, using standard solution processed methods.
PEG24) do not limit device performance. However, removing all
as it has been reported that small amounts of inert media (e.g.
ingress but residual solvent is not expected to limit PV efficiency
been investigated by SEM (ESI, S12) suggest that some terpineol may
remain after heating but terpineol acts as a solvent for crystallization it should slow H2O
proximally located on the surface. As further phase separation
CH3NH3X
separation into PbX2 and CH3NH3X but that both materials
remain on the surface. Hence, in the early stages of degradation,
the process can be reversed by heating at 100 °C. However, this
reversibility is only possible when the PbX2 and CH3NH3X are
proximally located on the surface. As further phase separation
occurs with time, this process becomes irreversible by heating.
However, it can be reversed by drying, grinding and heating to
re-mix the PbX2 + CH3NH3X. Here, we believe that the stabilising
influence of the Al2O3 is to slow the rate of phase separation and,
in doing so, effectively to shift the equilibrium (PbX2 + CH3NH3X ⇄ CH3NH3PbX3)
towards perovskite. Interestingly, Al2O3 capping layers on the perovskite absorber layer have also
been reported as moisture barriers. TGA data (ESI,† Fig. S11 and S12) suggest that some terpineol may remain after heating but that
this reduces with increasing temperature and/or time. If terpineol acts as a solvent of crystallization it should slow H2O
ingress but residual solvent is not expected to limit PV efficiency as it has been reported that small amounts of inert media (e.g. PEG) do not limit device performance. However, removing all
terpineol does not reduce film lifetime (ESI,† Fig. S12) suggesting surface perovskite:Al2O3 interactions may enhance film stability. In summary, we have demonstrated that photo-active, organo-
lead perovskites can be prepared by solid state reactions onto Al2O3 scaffolds producing materials with enhanced stability. Whilst this resolves key processing limitations by negating the need for toxic or
hygroscopic solvents such as DMF, GBL or DMSO, this approach also makes the synthesis of other (e.g. lead-free) organometallic perovskites much simpler as it avoids complex solvent engineering issues or complex solvent-solvent extraction techniques. In addition, using solid state reactions means that all the raw materials end up in the product which makes it easier to add trace components. Also the printing of pre-made perovskite inks is easily scalable whilst solution-based spin coating is not and the vast majority of precursor solutions are spun away making compositional control very difficult.

References