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


We report a solvent-free approach to synthesizing organolead perovskites by using solid state reactions to coat perovskite crystals onto Al$_2$O$_3$ or TiO$_2$ 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 architectures$^4$ including planar TiO$_2$ charge collection layers$^5$ and mesoporous TiO$_2$ as well as in batteries$^6$ and sensors$^7$. Electrically-insulating Al$_2$O$_3$ scaffolds$^8$ and even hole transporting-free perovskite devices$^9$ 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 current research. 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 coverage and avoiding the need for a perovskite capping layer. However, concerns remain over the solvents used for solution processed perovskites$^5$ 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%$^{12}$ which complicates scale up.

To date, the choice of perovskite processing solvent has been limited to dimethylformamide (DMF)$^2$, dimethylsulfoxide (DMSO)$^{13}$ or γ-butyrolactone (GBL)$^3$ given the need to dissolve the PbX$_2$ 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 PbX$_2$ and CH$_3$NH$_3$X react readily together with quantitative yield in solvent-free, solid state reactions by grinding/milling (ESI Fig. 1). We have also studied the addition of metal oxide nanoparticles (Al$_2$O$_3$ or TiO$_2$) 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 DMF$^{12}$ 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 $^\circ$C), which is similar to DMSO (189 $^\circ$C) which has been reported to stabilise solvent–PbI$_2$ complexes and inhibit PbI$_2$ crystallization$^{13}$. This also avoids the DMF volatalisation (b.p. 153 $^\circ$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 Al$_2$O$_3$, a loading of >10% Al$_2$O$_3$ is required to cast a uniform layer, presumably because Al$_2$O$_3$ acts as a plasticizer. This is more than the 5% Al$_2$O$_3$ reported by Carnie$^{14}$ et al. for their DMF/perovskite/Al$_2$O$_3$ nanoparticle precursor in their spin coating based study. The difference is that the perovskite particles are pre-formed on the Al$_2$O$_3$ 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 Al$_2$O$_3$ scaffold is their low-temperature processability. Thus, our inks can be deposited under ambient conditions and heated at 110 $^\circ$C because high temperature processing is not required to ensure inter-particle “necking” to carry electrical charge as is the case for TiO$_2$ photodeode$^{16}$. This is in line with previous reports for Al$_2$O$_3$ where heat processing is shown to be complete at 150$^\circ$C and 110$^\circ$C$^{14}$. The perovskite ink formulation is described in Equations 1 and 2.

$$[\text{PbX}_2 + \text{Al}_2\text{O}_3] + \text{CH}_3\text{NH}_3\text{X} \rightarrow [\text{CH}_3\text{NH}_3\text{PbX}_2:\text{Al}_2\text{O}_3] \quad \text{Eq. 1}$$

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

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For film deposition, a compact 80nm TiO$_2$ layer (Solaronix BL) was spin coated (3500rpm, 60s) onto TEC15 glass (15 $\Omega$sq$^{-1}$, NSG) and heated (550°C for 1h). 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 $\mu$m 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 Snaithe et al. original report of perovskite devices$^1$, 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$_2$ ($X = \text{Cl, Br, I}$) 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$_3$, an intermediate non-perovskite yellow phase is obtained (Fig. 1b) which only turns black and converts to perovskite after heating at 120 °C for 50min (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 Fig. 3). 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.

X-ray powder diffraction data show that the solid state reaction between CH$_3$NH$_3$I and PbI$_2$ produces predominantly the CH$_3$NH$_3$PbI$_3$ phase with only low intensity peaks observed for PbI$_2$ (Fig. 2b). Unconverted PbI$_2$ has been reported previously in the two-step

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**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.
suggesting variable particle sizes of perovskite crystals have been for samples deposited on optimally pre-heated (50°C) substrates, which is typically done to assist small particle formation and improve coverage13. 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 500nm particle sizes observed using the two-step method17. In addition for both ground samples, there is less evidence of preferred orientation (Fig. 2b-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 Cl, bar cast CH3NH3PbI3Cl and CH3NH3PbBr3 are all emissive, which suggests they should all be photo-active in PV devices (Fig. 3a-c). As expected, the thicker 7µm doctor bladed CH3NH3PbI3Cl film (Fig. 3a, f) shows PL intensity which is much greater than that of the equivalent 400 nm bar cast film (Fig. 3b, f).

Interestingly, the intensity of the doctor bladed film is comparable to the solution processed image (Fig. 3e, 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 CH3NH3PbI3Cl sample although at λ ca. 540nm 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. 600cps compared to ca. 12000cps for the doctor bladed and ca. 500000cps for the CH3NH3PbI3Cl 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 films22,23. Fig. 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 (i.e. typically <100 nm). Perovskite film morphology has also been investigated by SEM (ESI Figs. 5-8) which shows the best perovskite coverage for CH3NH3PbBr3 ink in line with the higher intensity PL data for this film.

The lifetime of the perovskite films has also been studied (Fig. 4). The data show that Al2O3-based films exhibit significantly better
solution processed films. We have observed that the first stage of resistance to atmospheric exposure (air, humidity, light) than drying, grinding and heating to re-mix the PbX surface. As further phase separation occurs with time, this process believe that the stabilising influence of the Al lead-free) organometallic perovskites much simpler as it avoids perovskite:Al do not limit device performance. However, removing all terpineol it has been reported that small amounts of inert media (e.g. PEG 10 10 that this reduces with increasing temperature and/or time. If 10 have also been reported as moisture barriers 3 that this reduces with increasing temperature and/or time. If 10 have also been reported as moisture barriers 3 3+ CH 3 NH 3 PbI 3↔CH 3 NH 3 PbX 3 is to slow the rate of phase separation and, in doing so, effectively to shift the equilibrium (PbX 3 + CH 3 NH 3 X ↔ CH 3 NH 3 PbX 3 towards perovskite. Interestingly, AlO 2 capping layers on the perovskite absorber layer have also been reported as moisture barriers 10 . TGA data (ESI Fig. 11, 12) 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 H 2 O 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 10 ) do not limit device performance. However, removing all terpineol does not reduce film lifetime (ESI Fig. 12) suggesting surface perovskite:AlO 2 interactions may enhance film stability.

In summary, we have demonstrated that photo-active, organo-functionalized perovskites can be prepared by solid state reactions onto AlO 2 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 26 or complex solvent-solvent extraction techniques 26 . 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