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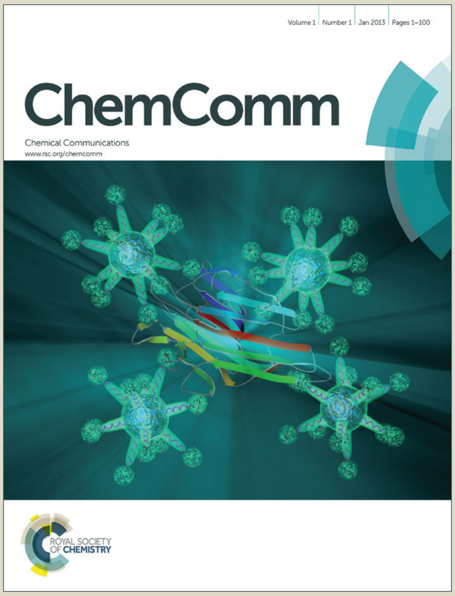

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# Ambient Pressure Aerosol-Assisted Chemical Vapour Deposition of $(CH_3NH_3)PbBr_3$, an Inorganic-Organic Perovskite Important in Photovoltaics

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**The inorganic-organic perovskite $(CH_3NH_3)PbBr_3$, which is potentially important in photovoltaics, has been deposited using aerosol-assisted chemical vapour deposition (AACVD).**

Solid state solar absorbers such as tin sulfide (SnS),[1] copper zinc tin sulfide (CZTS)[2, 3] and copper indium gallium sulfide (CIGS),[4] which show excellent absorption characteristics over the solar radiation spectrum, are potentially cheaper to produce than silicon-based photovoltaic devices and potentially can give power conversion efficiencies commensurate with planetary demand, representing good candidates for next generation solar cells, with the full potential of these materials not yet realized. Dye sensitized solar cells (DSSCs), popularized by Grätzel and co-workers[5] currently show power conversion efficiencies (PCEs) of 10-15%,[6] but have also suffered problems with their reproducibility and long-term use.[7] Quantum dots have also been investigated as light harvesting materials for solar cells and show great promise through multiple exciton generation phenomena as well as the ability to tune the absorption wavelength by using quantum confinement effects.[8-10]

Inorganic-organic perovskites (IOPs) such as $(CH_3NH_3)PbX_3$ (X = Cl, Br, I) have recently attracted considerable interest as an absorbing layer for solar energy conversion applications.[11, 12] $(CH_3NH_3)PbBr_3$ adopts the classic inorganic perovskite structure ($ABX_3$) with a cubic arrangement of eight $CHNH_3^+$ cations with face-centering by six $Br^-$ anions, and a lead(II) ion positioned at the centre of the unit cell (Figure 1). The visible light sensitization properties of IOPs were first reported by Miyasaka and co-workers, with PCEs in a solar cell containing the IOP deposited onto $TiO_2$ of ca. 3-4%. Recent PCEs for IOP perovskite sensitised solar cells reported by Grätzel and co-workers and Snaith and co-workers are ca. 15%.[13, 14] In the latter study mixed-halide perovskites ($(CH_3NH_3)PbI_{3-x}Cl_x$) were deposited by chemical vapour deposition (CVD) onto $TiO_2$ substrates under high vacuum from dual organic ($CH_3NH_3I$) and inorganic ($PbCl_2$) sources. Bisquert and co-workers have recently highlighted that IOPs perform equally as well whether deposited on nanostructured substrates or as thin films.[15] Kanazidis and co-workers have recently replaced the Pb(II) centres with Sn(II) centres.[16] Due to their salient properties for solar energy conversion, including step-change PCEs that are still relatively un-optimised combined with their inexpensive and earth-abundant constituent elements, IOPs have been rightly heralded as a potential 'game-changer' in sustainable photovoltaics.[6]

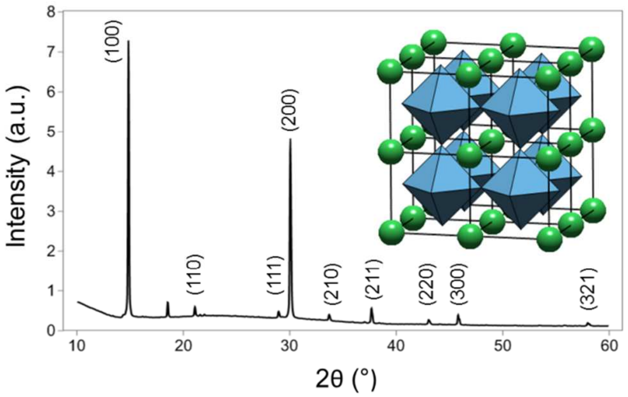

**Fig. 1** PXRD pattern of a $(CH_3NH_3)PbBr_3$ thin film deposited by AACVD at 250°C. Inset: the structure of inorganic-organic perovskites ($ABX_3$) of the form $(CH_3NH_3)PbBr_3$, methylamines represented as spheres with $PbBr_3$ polyhedra.

In this communication we report the deposition of thin films of an IOP, $(CH_3NH_3)PbBr_3$ onto glass substrates using aerosol assisted chemical vapour deposition (AACVD) from a single precursor solution. AACVD has attracted attention as it is an ambient-pressure CVD technique that uses nebulization of precursor molecules, followed by transport of the aerosol by an inert carrier gas such as argon to a substrate surface where thermal decomposition of the precursor occurs. AACVD has been used for the deposition of various semiconductors including $MoS_2$,[17] SnS[1, 18] and CZTS.[2] AACVD is a very attractive deposition technique as it occurs under ambient pressure, the apparatus required is relatively simple and inexpensive and amongst the range of CVD techniques available it has very good potential for scale-up.[19] Furthermore it requires precursors with only moderate volatility, extending the range of molecules that can be employed for the deposition of thin films. To the best of our knowledge, AACVD has never been used for the deposition of IOP thin films.

The lead(II) precursor $(CH_3NH_3)PbBr_3$ was prepared by reaction of methylamine with hydrobromic acid followed by crystallization of the hydrobromide salt, $CH_3NH_3Br$ by reduction of the volume *in vacuo*. Lead(II) bromide ($PbBr_2$) was then mixed in stoichiometric ratio with the methylamine hydrobromide in *N,N*-dimethylformamide (DMF) and heated at 60 °C for 2 hours.[20] The DMF solution is then diluted tenfold with acetonitrile (minor precipitation was observed here, solids were removed). The diluted precursor solution is then nebulized using a commercial humidifier and the aerosol is carried into a hot tube furnace (250 °C) containing a glass substrate by a stream of argon (200 sccm). Thermal decomposition of the precursor on the substrate occurs to leave a striking yellow-orange film of $(CH_3NH_3)PbBr_3$. Powder X-ray diffraction (PXRD) measurements on the as-deposited film gave major diffraction peaks at $2\theta = 14.77°$ and $29.98°$ (Figure 1) corresponding to the (100), and (200) planes of a cubic perovskite unit cell ($Pm\bar{3}m$) with a lattice constant of 5.9 Å, as expected and consistent with previous work with solution deposited material.[11, 21] In addition to this minor Bragg reflections from (110), (111), (210) (220), (300) and (321) planes were observed, thus confirming the crystalline nature of the deposited $(CH_3NH_3)PbBr_3$.

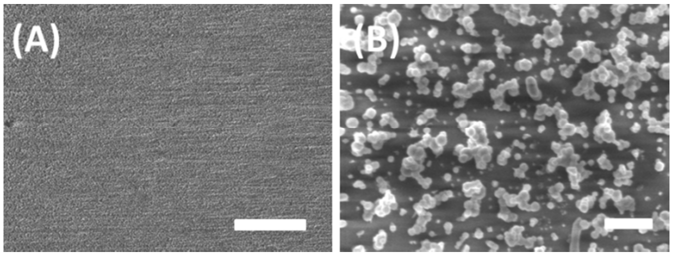

**Fig. 2** Secondary electron SEM micrographs of a $(CH_3NH_3)PbBr_3$ thin film deposited by AACVD at 250 °C. (A) Image taken at 6 keV, 500 × magnification, showing the uniformity of coverage. The scale bar corresponds to 50 µm. (B) Image taken at 6 keV, 8000 × magnification revealing the crystalline appearance of deposited $(CH_3NH_3)PbBr_3$. The scale bar corresponds to 2 µm.

The morphology of the as-deposited films was investigated by scanning electron microscopy (SEM, Figure 2), with images taken in secondary electron mode at 6 keV beam voltage. Wide-field SEM images show a uniform coating of $(CH_3NH_3)PbBr_3$ across the glass substrate, comparable in uniformity to such IOPs as deposited by high-vacuum CVD.[14] Images taken at higher magnification revealed the crystalline appearance of the perovskite on the glass. Energy-dispersive analysis of x-ray spectroscopy (EDX) of the film as-imaged revealed a Pb:Br atomic ratio of around 1:3 as expected for $(CH_3NH_3)PbBr_3$. The consistent coating of the sample across an interrogation area of ca. 25 × 25 µm was confirmed by quantitative EDX mapping at 25 keV (Figure 3); the distribution of both Pb and Br is uniform over the interrogated area at a resolution of ca. 1 µm.

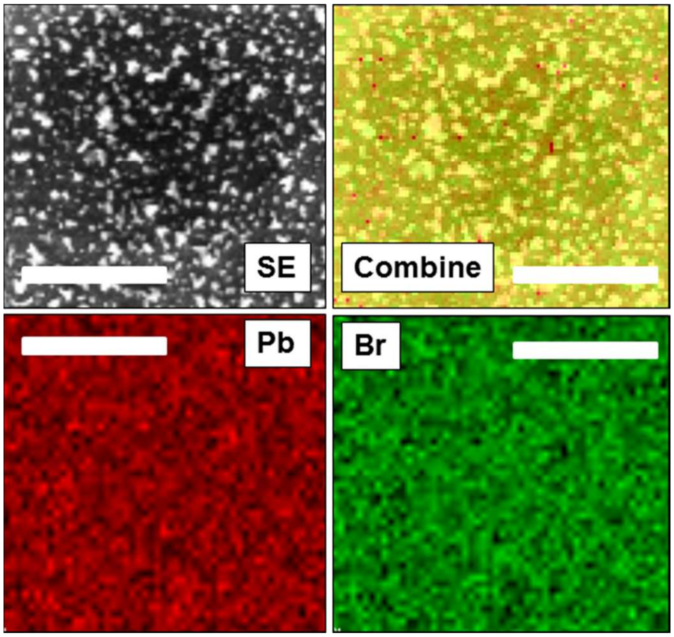

**Fig. 3** EDX (25 keV) Q-maps demonstrating the uniform coverage of $(CH_3NH_3)PbBr_3$ films over a region of interest of ca. 25 × 25 µm. All scale bars correspond to ca. 10 µm. Q-mapping of the Pb (Lβ, 10.6 keV) and Br (Kα, 11.9 keV) channels show a uniform coverage of both elements. Combination of the Pb and Br Q-maps overlayed with the secondary electron (SE) SEM image of the area generates a yellow colour revealing the co-localisation of both elements across the entire region.

## Conclusions

We have used aerosol-assisted chemical vapour deposition (AACVD) to produce films of the light-harvesting perovskite $(CH_3NH_3)NH_3Br_3$ on glass substrates. The use of AACVD to deposit such materials is an exciting development due to the simple apparatus required for AACVD combined with its great potential for scale-up, an essential requirement for any solution to the alternative energy question. The films produced by this method are comparable in quality to current methods used for deposition of IOPs such as spin coat – annealing and furthermore do not require high vacuum for their deposition.

## Notes and references

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Electronic Supplementary Information (ESI) available: synthetic procedures and full description of AACVD conditions. See DOI: 10.1039/c000000x/

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