# Optic Fibre Sensor for the Detection of Gaseous Ammonia with Lead Halide Perovskite

## Electronic Supplementary Information (ESI)

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### Water influence on perovskite sensor

The sensor was exposed to moisture by simply placing the probe above a bottle of water for a short of time, the PL intensity was quenched by 32 % and then recovered with the remove of water indicating the interaction between perovskite crystals and water molecules was reversible (Fig. S1). This was consistent with the reported $MAPbBr_3$ applied as humidity sensor, and the incorporation of a water molecule into the perovskite is primarily driven by hydrogen bonds between water molecules and halides.[1]

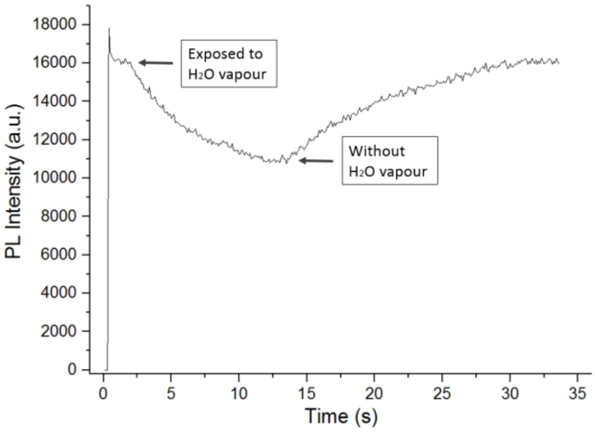


**Fig. S1** The reversible PL intensity change of $MAPbBr_3$ immobilised optical probe was quenched when exposed to water vapour and then recovered with the remove of water.

Likewise, $MAPbBr_3$ crystal was thoroughly washed with Milli-Q water and the crystal morphology was observed changing from orange cubic to white rod-shape $MAPbBr_3$-$H_2O$ crystal (see Fig. S2 for optical image), these white rod-shape crystals were then annealed at 100 °C for 20 min. XRD pattern shows that main peaks of $MAPbBr_3$ (black line in Fig. 9A) at $2\theta = 14.9°$, 30.2° and 45.9°, which confirms the cubic structure of $MAPbBr_3$ single crystal, and is consistent with the previously reported data.[2] In the presence of bulk water, a tendency of liquid water to transform perovskite structure was observed through the disappearance of diffraction peak at $2\theta = 14.9°$ and deterioration of crystallinity due to the low diffraction intensity. It was reported that water can isolate MA and halide in perovskite and producing insoluble lead halide.[3] However, neither MABr nor $PbBr_2$ were identified in the water treated $MAPbBr_3$ crystal through XRD analysis (Fig. 9B) and the exact intercalated phases between $MAPbBr_3$ and bulk water need further investigation, which is beyond the range of this study.

It should be noted that interaction mechanism of perovskite with water vapour and its full dissolution in liquid water are different. At room temperature the water vapour absorption is energetically favoured and the water molecules can diffuse without damaging the crystal structure. On the contrary, the dissolution of perovskite such as $MAPbI_3$ in liquid water is irreversible[3], and hydrogen bonding between water molecules and the methylammonium cations leads to transformation of the 3D perovskite structure into 2D sheets separated by water molecules[4].

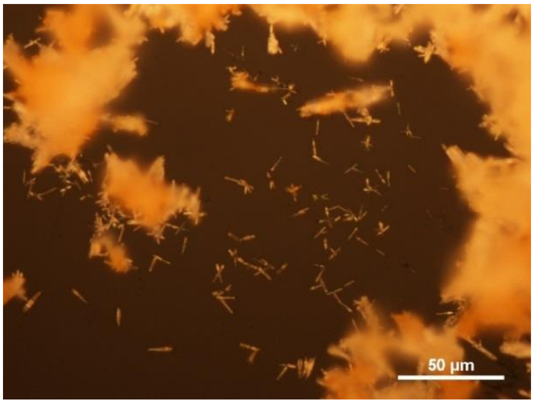


**Fig. S2** The optical image of $MAPbBr_3$ crystal after wash with Milli-Q water.

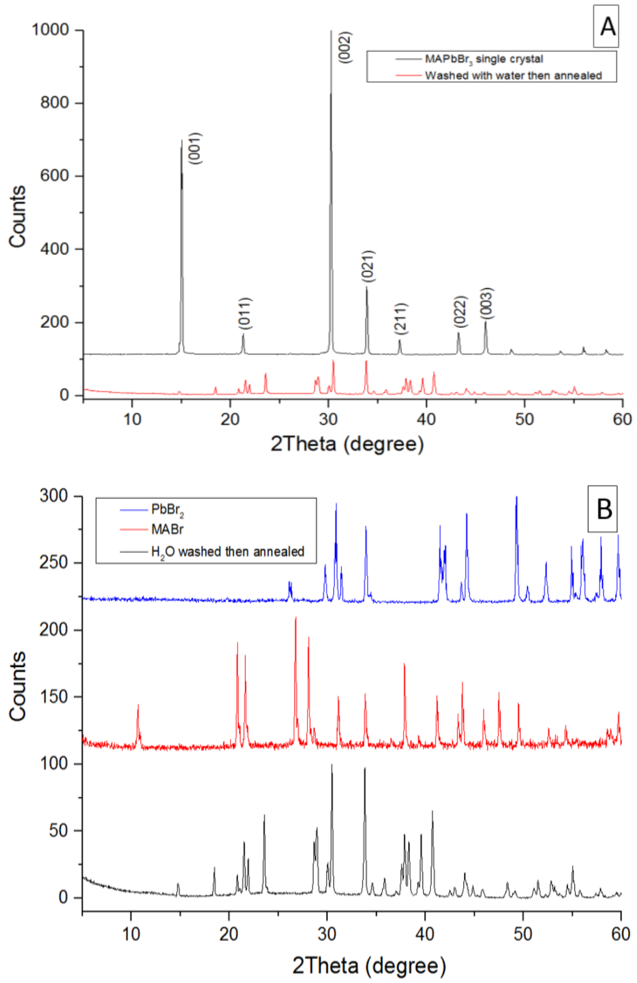
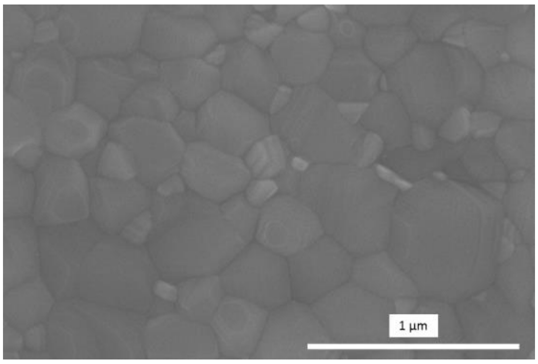


**Fig. S3** XRD patterns of Milli-Q water washed $MAPbBr_3$ single crystal (A) compared with $PbBr_2$ and $MAPbr_2$ powder (B).



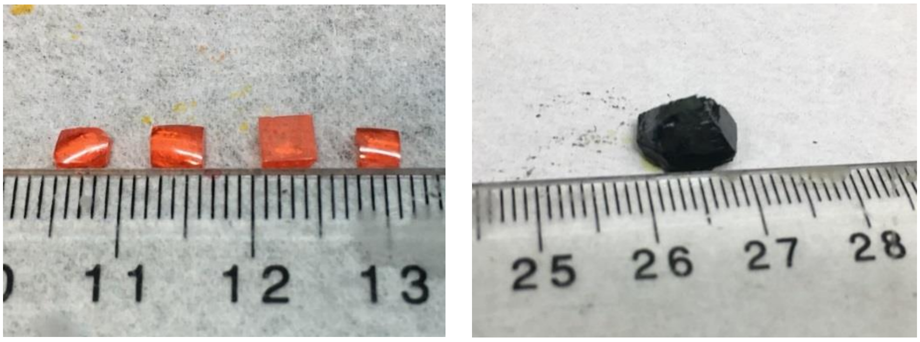


**Fig. S4** The SEM top view of the MAPbBr$_3$ film deposited by the anti-solvent method, the film with densely packed grains with sizes ranging from 100 to 500 nm (top). Images of synthesised MAPbBr$_3$ (bottom left) and MAPbI$_3$ (bottom right) single crystal.

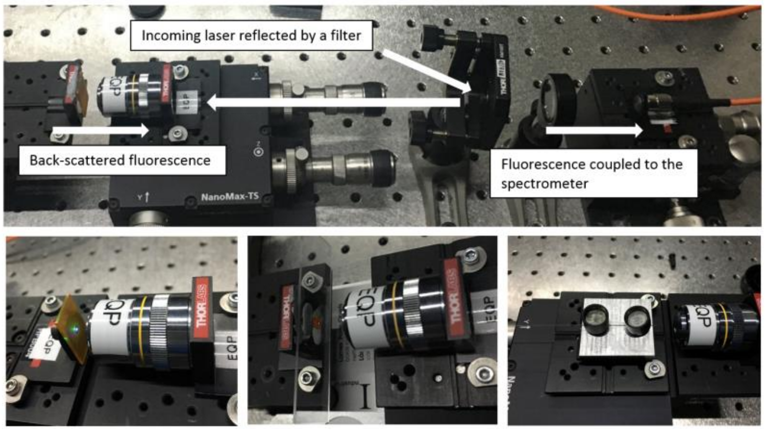


**Fig. S5** Experimental setup for the perovskite photoluminescence detection (Above). Signal collected from polycrystalline film, single crystal and optic fibre (Below, from left to right).

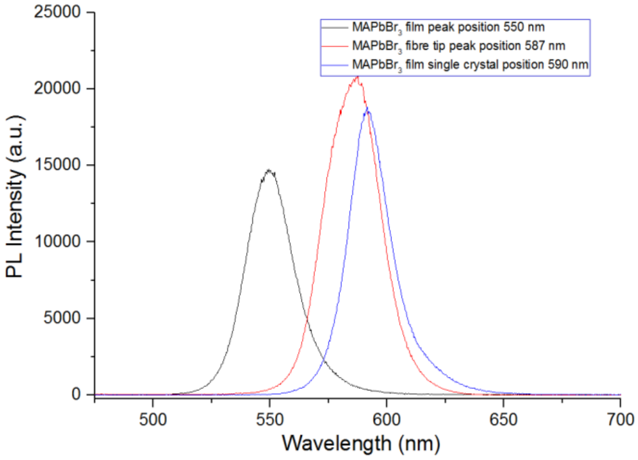


**Fig. S6** PL spectrum of MAPbBr$_3$ film, micro size crystal and centimetre size single crystal.

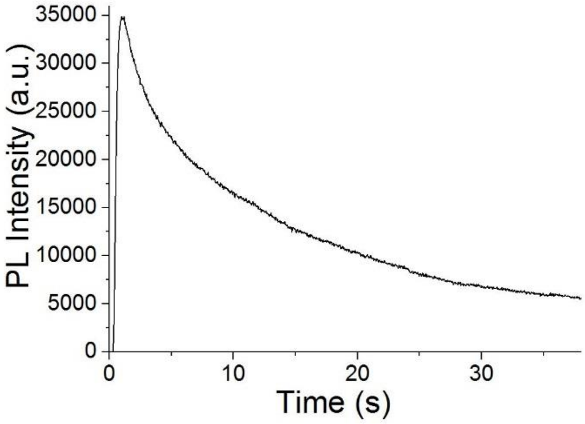


**Fig. S7** Laser induced relaxation effect for $MAPbI_2Br_1$ film.

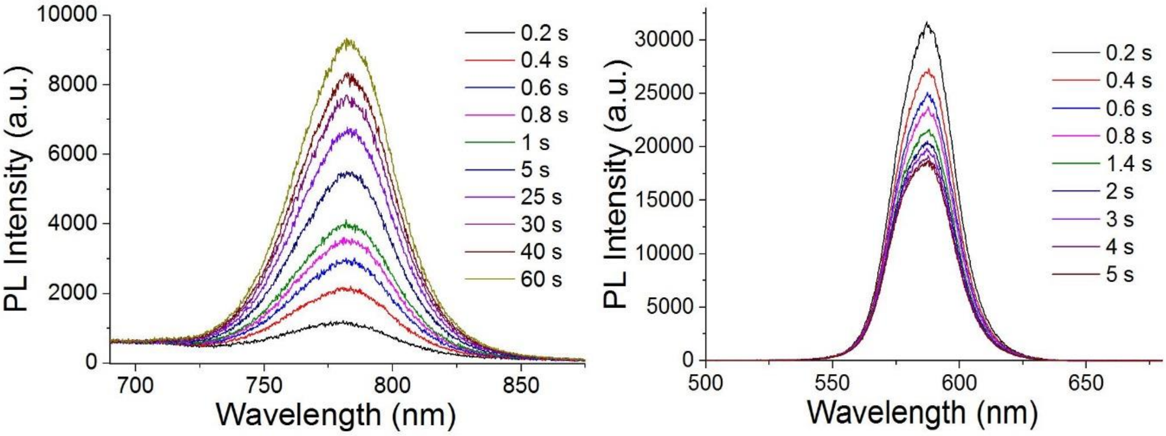


**Fig. S8** Laser induced PL intensity enhancement for $MAPbI_3$ (left) and relaxation effect for $MAPbBr_3$ (right) single crystals.

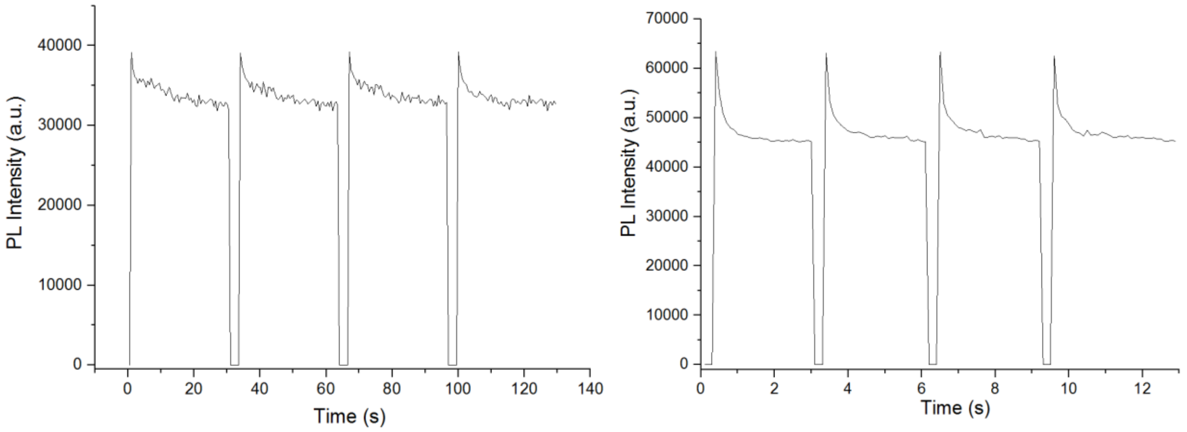


**Fig. S9** Laser induced relaxation effect for $MAPbBr_3$ film (left) and micro size $MAPbBr_3$ crystal (right) immobilised on fibre tip.

Fig. S8 shows the quenching of PL in films of $MAPbI_3$, $MAPbBr_3$ and $FAPbBr_3$ by ammonia gas. Simply, the film is keep illuminated with 1 mW 407 nm laser until a stabilised PL intensity was achieved, a bottle with 3 wt.% ammonia solution was then moved right below the film, the evaporated ammonia molecules were then react with perovskite and the decreased PL intensity was in-situ recorded by a spectrometer.

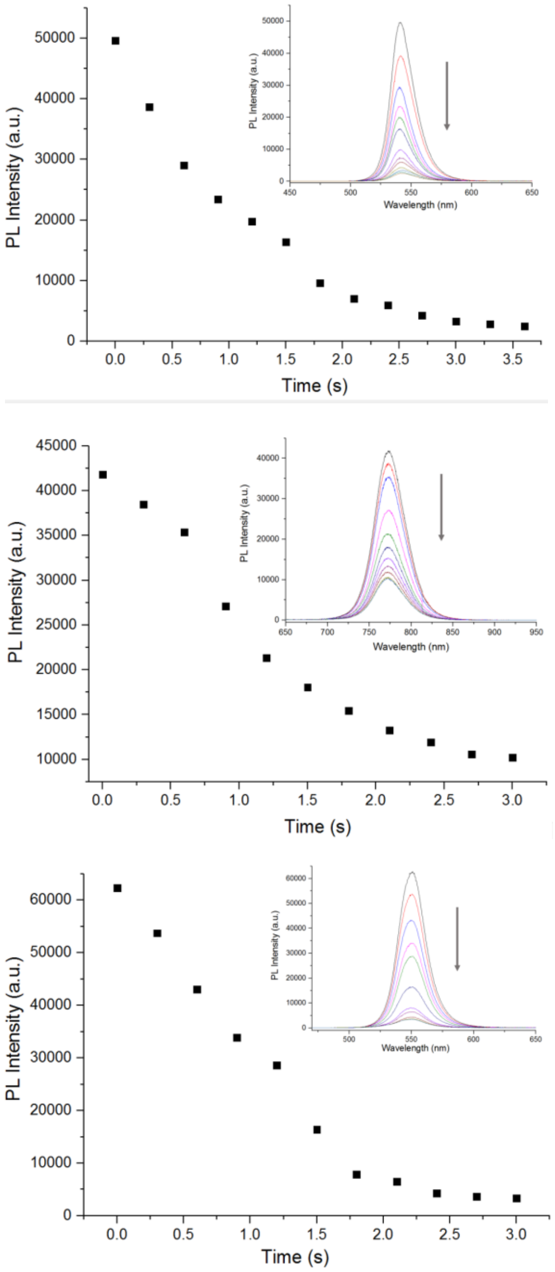


**Fig. S10** In situ monitoring of PL quenching process of FAPbBr$_3$ (above), MAPbI$_3$ (middle) and MAPbBr$_3$ (below) films when exposed to 3 wt.% aqueous ammonia solution.

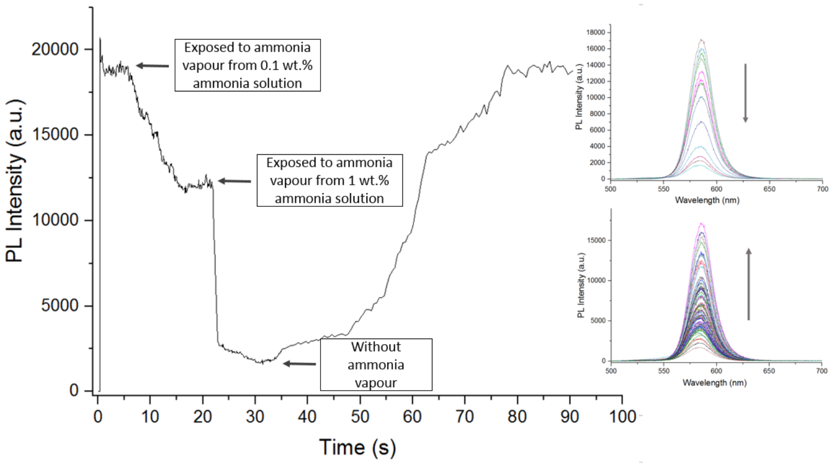


**Fig. S11** The sequential detection by initially expose to 0.1 wt.% and then 1 wt.% ammonia solution.

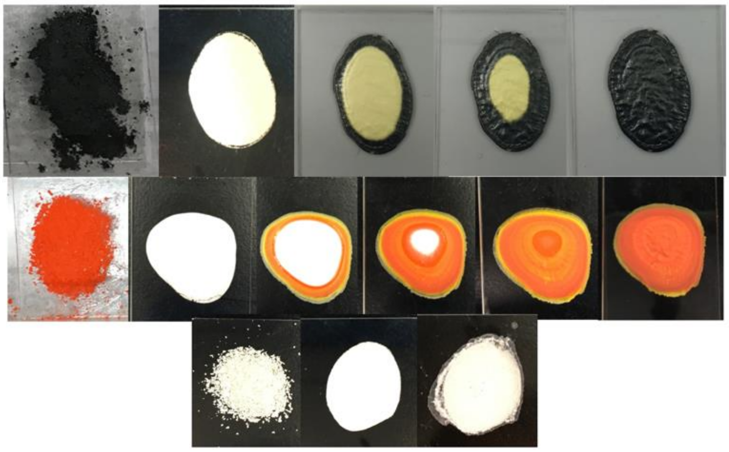


**Fig. S12** Perovskite single crystal ($MAPbI_3$, $MAPbBr_3$ and $MAPbCl_3$ from top to bottom) changed to white after ammonia wash and gradually reversed upon annealed at 100 °C for 5 min.

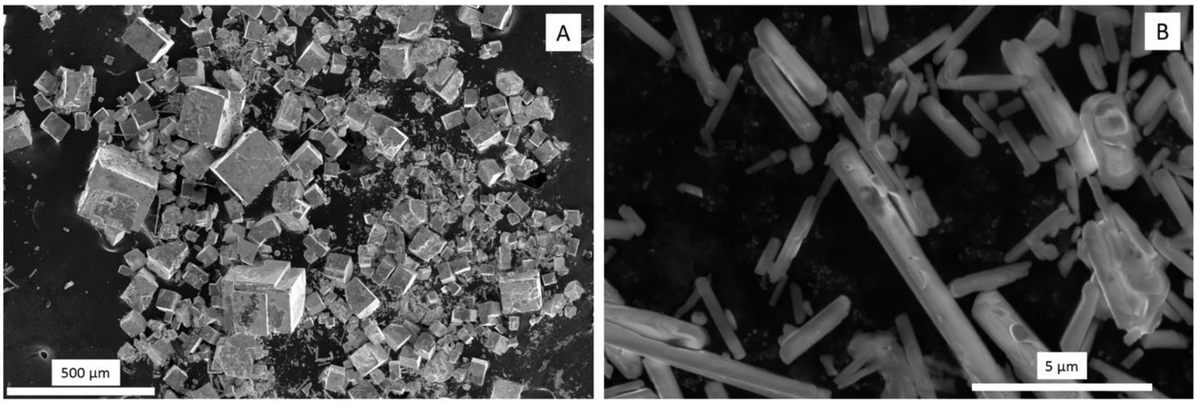


**Fig. S13** SEM image of $MAPbBr_3$ single crystal and its morphology after ammonia treatment.

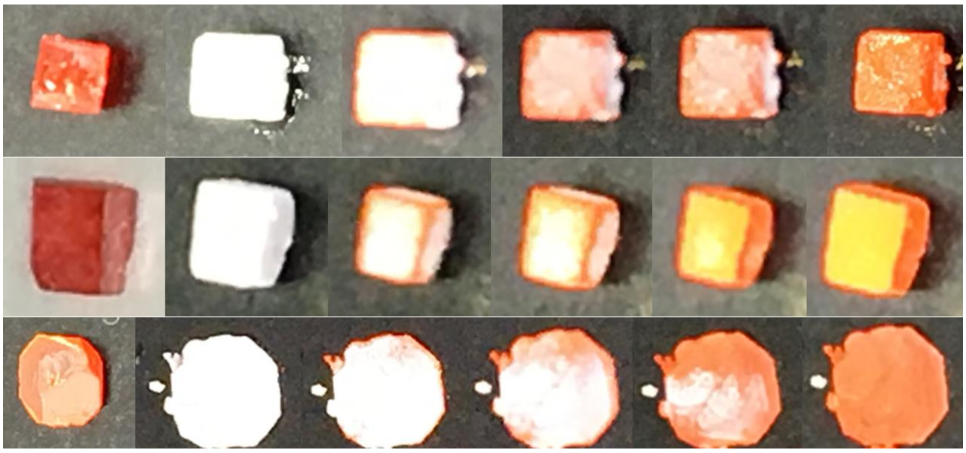


**Fig. S14.** Recovery of colour in mm-sized $MAPbBr_3$ crystals after treatment in ammonia solution without annealing.

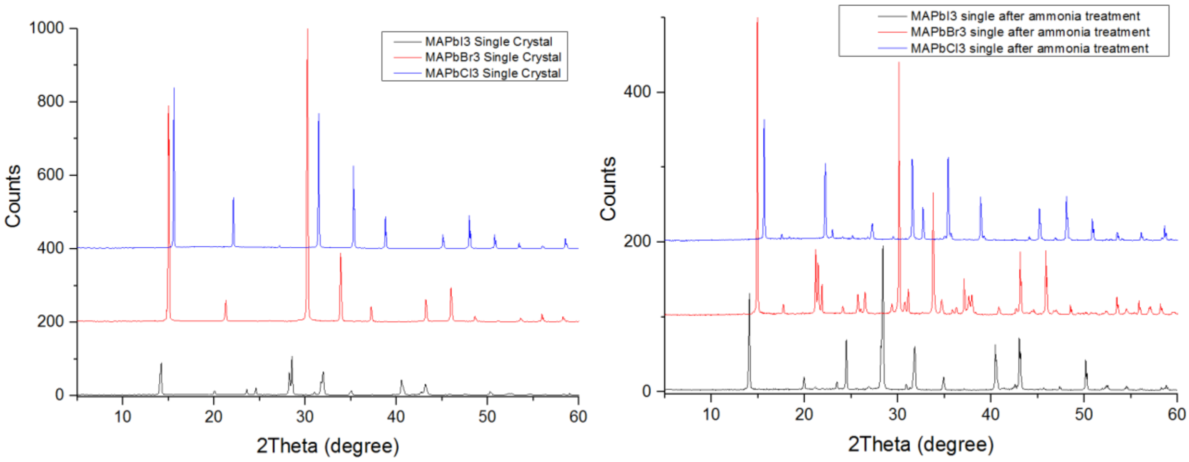


**Fig. S15** The X-ray diffraction pattern compare of methylammonium lead halide before (left) and after (right) the treatment of ammonia.

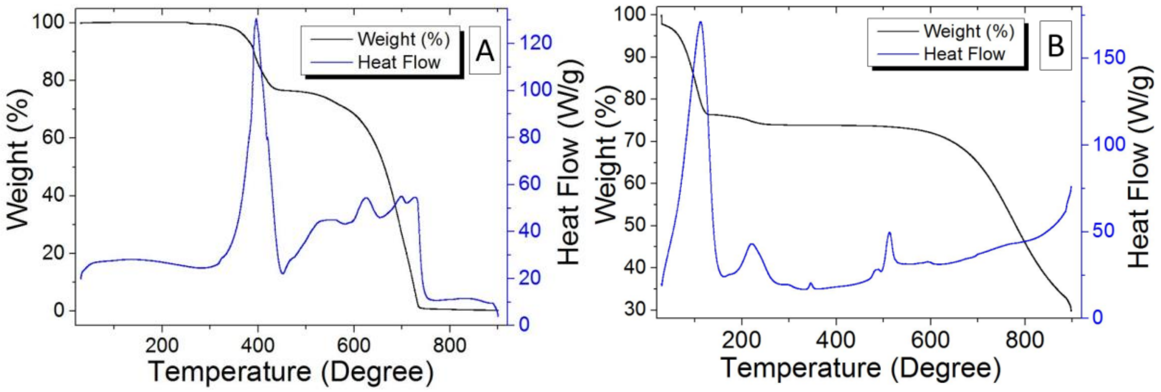


**Fig. S16** The DTA thermal curve and the TGA weight loss curve for $MAPbBr_3$ (A) and $NH_4PbX_3 \cdot MA$ (B).

1 W. Xu, F. Li, Z. Cai, Y. Wang, F. Luo and X. Chen, *Journal of Materials Chemistry C*, 2016, **4**, 9651.

2 D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger and K. Katsiev, *Science*, 2015, **347**, 519.

3 C. Caddeo, M. I. Saba, S. Meloni, A. Filippetti and A. Mattoni, *ACS nano*, 2017, **11**, 9183.

4(a) A. l. M. Leguy, Y. Hu, M. Campoy-Quiles, M. I. Alonso, O. J. Weber, P. Azarhoosh, M. Van Schilfgaarde, M. T. Weller, T. Bein and J. Nelson, *Chemistry of Materials*, 2015, **27**, 3397; (b) F. Hao, C. C. Stoumpos, Z. Liu, R. P. Chang and M. G. Kanatzidis, *Journal of the American Chemical Society*, 2014, **136**, 16411.