Electronic Supplementary Material (ESI) for Nanoscale.
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Supplementary Information

Influence of growth temperature on bulk and surface defects in hybrid lead halide perovskite films

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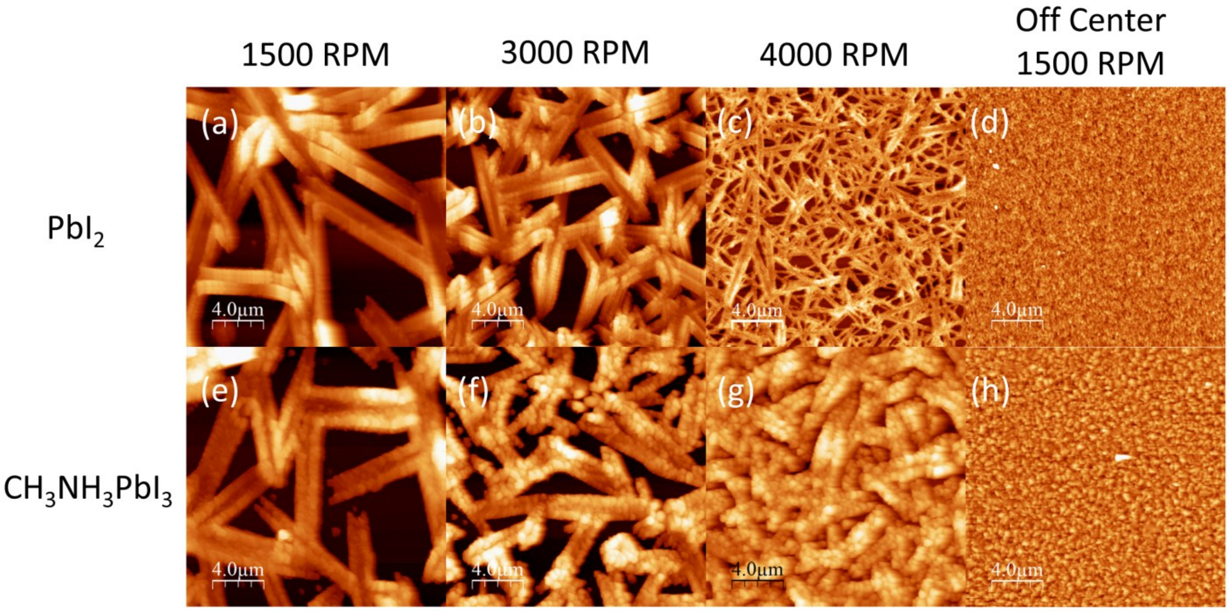

Figure S1 AFM images (10×10 μm) of the as spinned PbI_2 surfaces ((a), (b), (c) and (d)) and the corresponding converted perovskite surfaces ((e), (f), (g) and (h)) for various spin positions and spin speeds. The conversion is implemented at 175°C for an hour. (a-c) is prepared with the substrate positioned at the center. Fiber shaped large crystals of PbI_2 are observed for all the spinning speeds, although the crystals become finer and denser with increasing spin speed. The morphology remains unchanged even after the conversion because of the template effect associated with VASP. Smooth and uniform morphology is obtained only when the substrate is positioned a little away from the center as shown in (d).

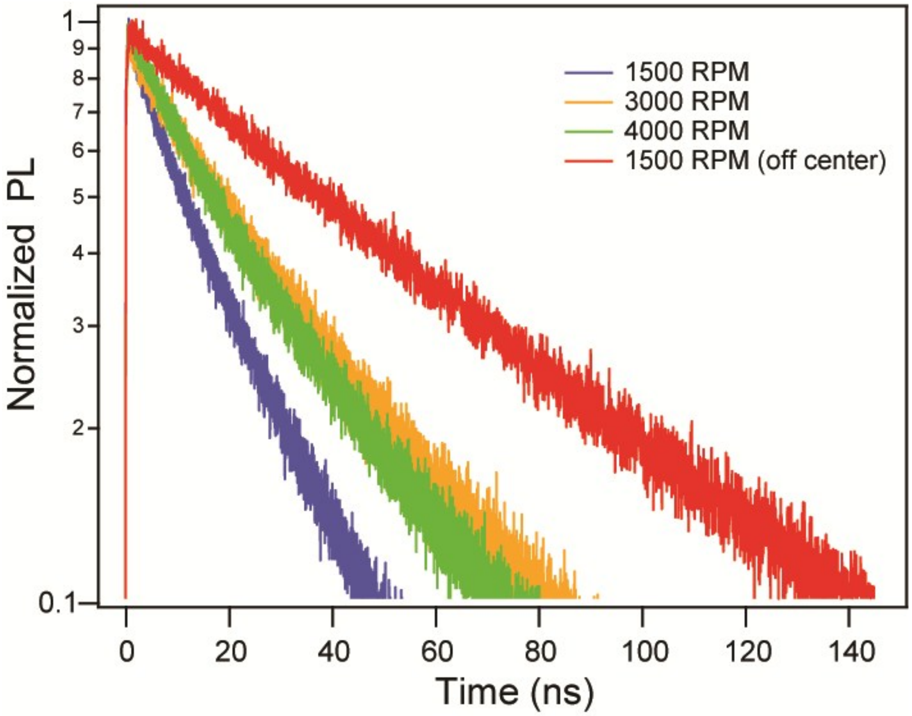

Figure S2 Time-resolved photoluminescence (TRPL) decay curves for the perovskite samples shown in Fig. S1 (e), (f), (g) and (h) under an excitation fluence of 0.36 µJ/cm^2. Clearly, the surface morphology affects the TRPL decay.

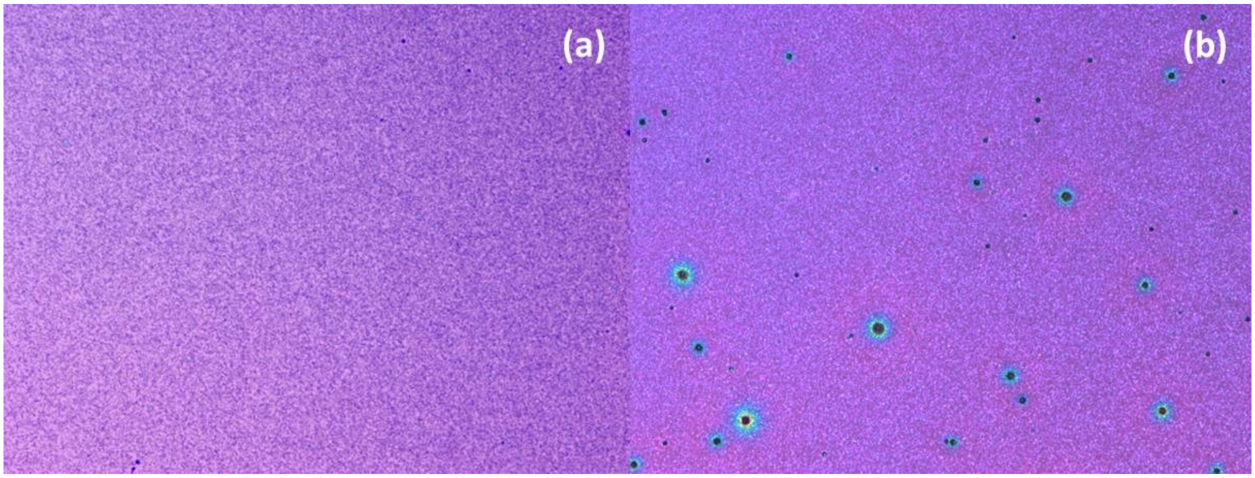

Figure S3 Optical microscopic images of a) 150^{o}C and b) 200^{o}C samples depicting the formation of pin holes at higher temperature. These defective spots are intentionally avoided during the PL measurements.

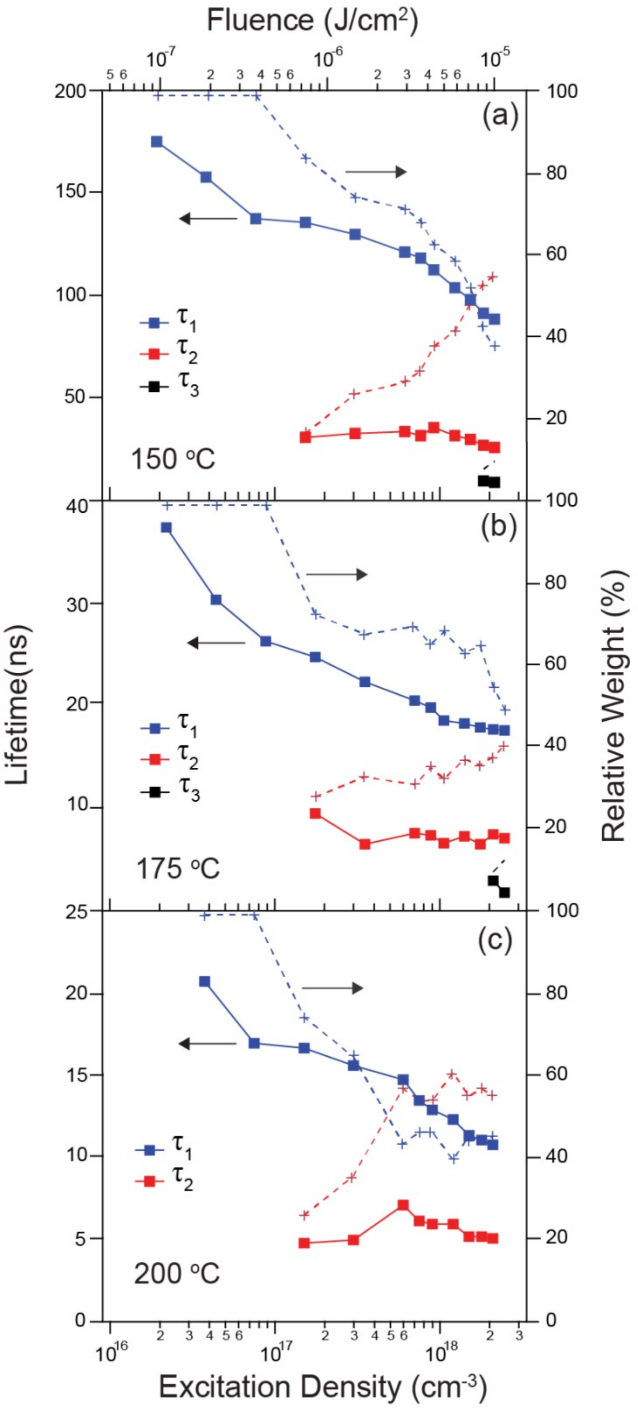

Figure S4 PL lifetimes (solid symbols, left axis) and the corresponding weights (+ symbols, right axis) as a function of excitation density are shown for samples grown at (a) 150°C, (b) 175°C and (c) 200°C, respectively. τ_1, τ_2 and τ_3 correspond to multi exponential fits representing different recombination mechanisms viz. monomolecular, bimolecular and auger recombination which are characterized by considerably different decay rates [25].

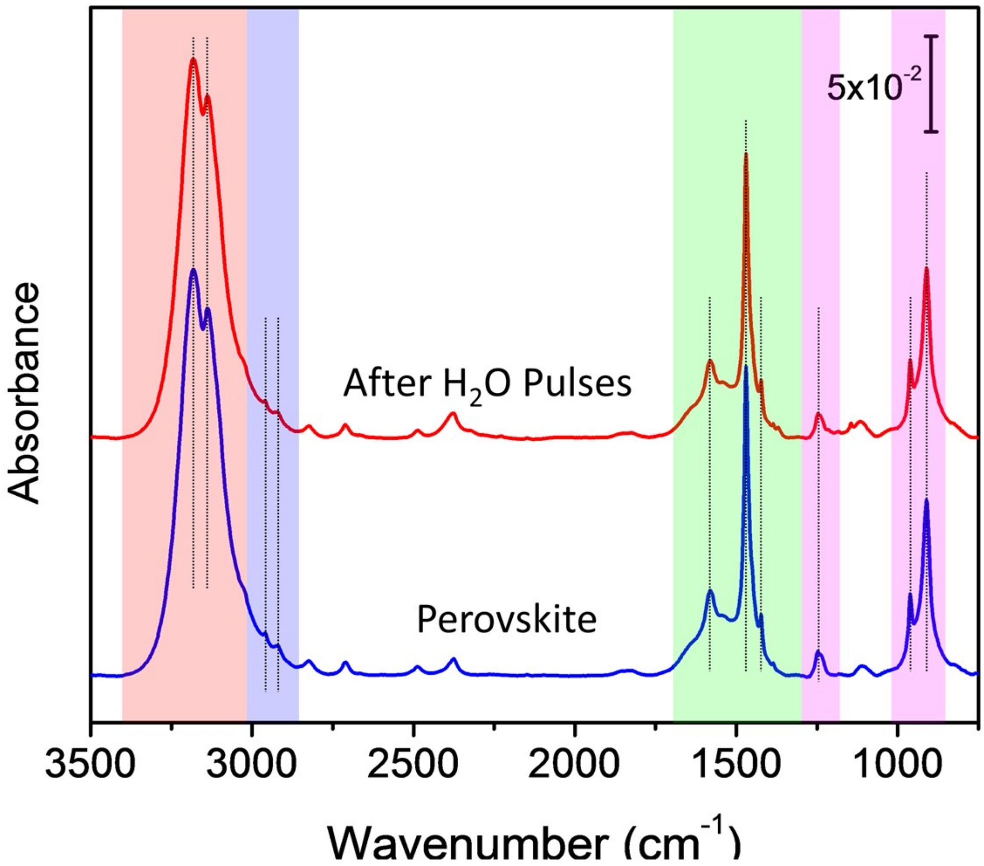

Figure S5 Room temperature FTIR spectra of the perovskite sample before and after the treatment with several water pulses. The water treatment was performed in a home-built reactor chamber equipped with *in situ* FTIR capabilities. The perovskite sample was deposited on one side of a double-side polished Si substrate with 3 nm of thermal oxide. Most of the vibrational modes come from the organic cations, with the spectral regions marked in red (3181 cm^{-1}, 3137 cm^{-1}), blue (2959 cm^{-1}, 2921 cm^{-1}), green (1581 cm^{-1}, 1470 cm^{-1}, 1423 cm^{-1}) and pink (1493 cm^{-1}, 961 cm^{-1}, 910 cm^{-1}), corresponding to the N-H stretching, C-H stretching, NH_3 and CH_3 deformation and C-N rocking and stretching modes, respectively. Both the peak position and intensity remain almost the same even after the water treatment indicating that the majority of the organic cations within the perovskite, except for those near the surface region, are not perturbed after the water treatment.

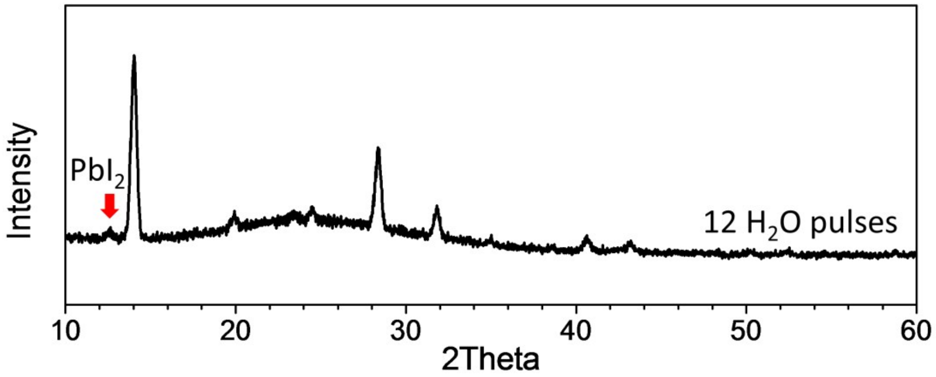

Figure S6 XRD spectrum of the 200°C annealed perovskite sample treated with 12 water pulses. The small peak at 12.6° (indicated by the red arrow) corresponds to the formation of PbI_2 phase which is absent in 2-8 water pulse treated samples.

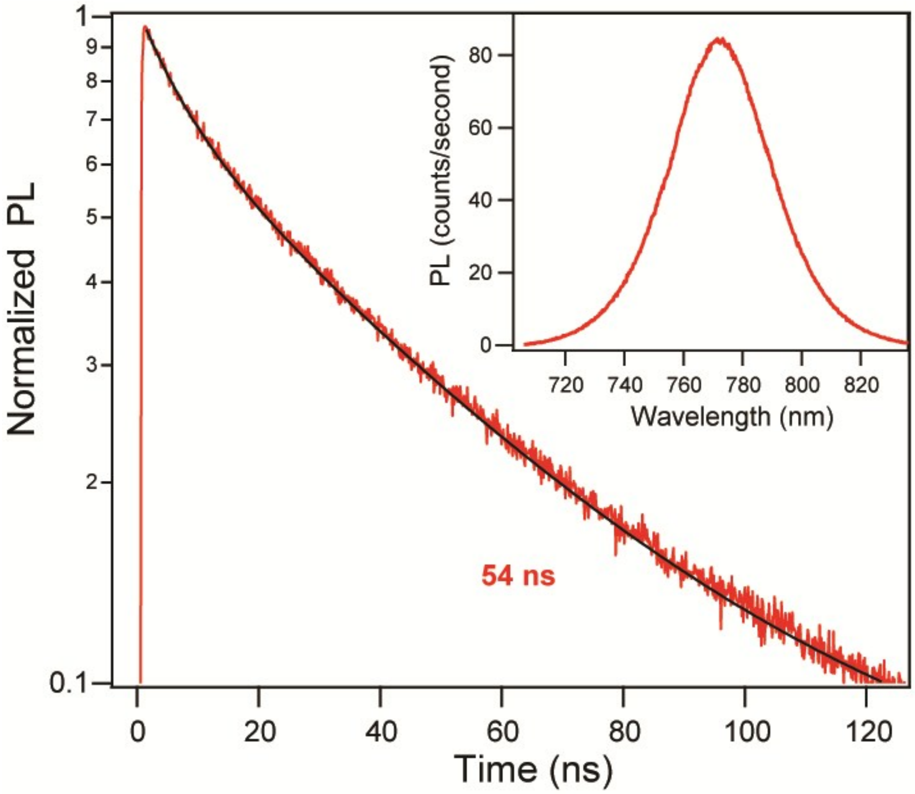

Figure S7 PL spectrum (inset) and TRPL decay curve of the 200°C annealed sample treated with 12 water pulses. The lifetime is further increased to 54 ns compared to the samples treated with 2-8 water pulses (33-39 ns).

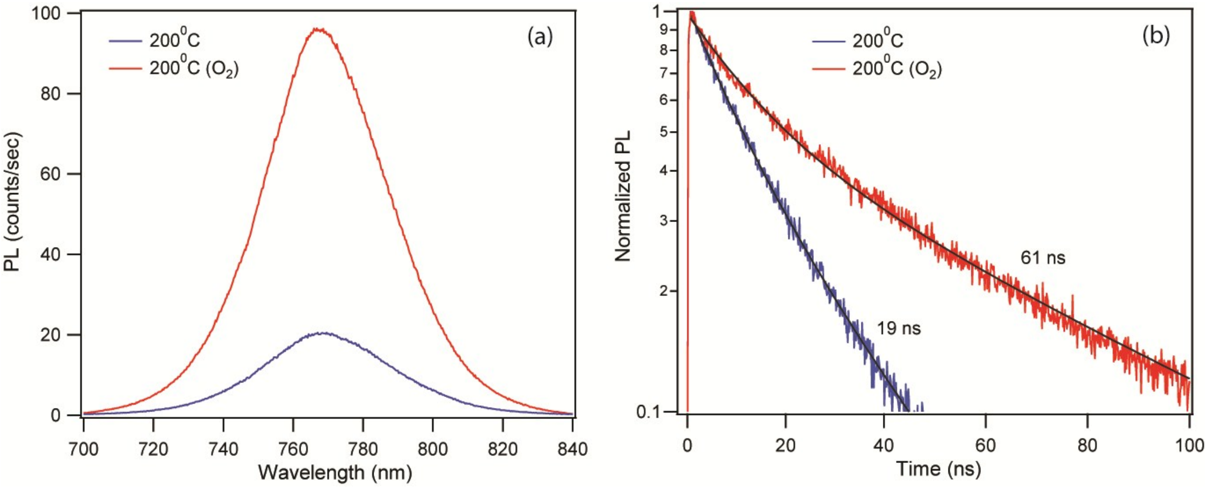

Figure S8 PL a) intensities and b) lifetimes of 200°C-grown sample prepared in N_2 and O_2 environments. Synthesis under O_2 exposure leads to a ~3 fold increase in the PL intensity and lifetime, in agreement with recent findings that O_2 mediated trap passivation via photochemical reaction [22]. However the lifetime of O_2 treated 200°C annealed sample (61 ns) is still lower than the 150°C annealed sample (111 ns). The extent of the enhancement here is higher compared to the ~2 fold increase observed (14 ns to 33 ns) when the perovskite surface is selectively passivated with H_2O pulses, as described in the manuscript. It is important to note that, by the nature of the treatment followed here, H_2O passivation is restricted mainly to the surface, whereas the O_2 passivates both the surface and bulk traps (as reported in Ref. 22) as the synthesis is carried out in O_2 rich environment. Thus the current findings provide additional confirmation to the existence of bulk traps in perovskites. However more systematic studies are required in order to specifically quantify the degree of passivation of bulk and surface traps, and the exact passivation mechanisms, which are beyond the scope of the current study.