Supporting Information

Interaction of the Cation and Vacancy in Hybrid Perovskites Induced by Light Illumination

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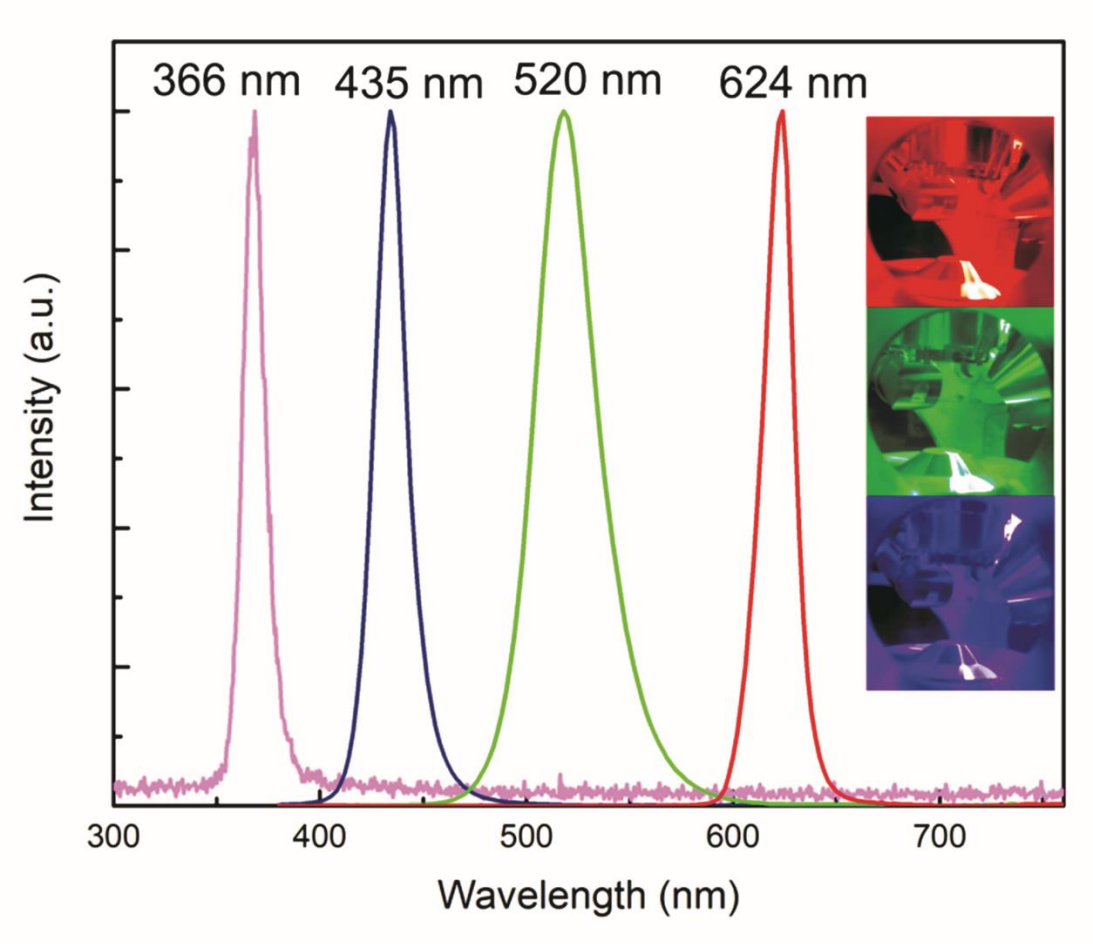

Figure S1. The electroluminescence spectra of four light sources used in the experiments. The insets show the photographs taken from the *in-situ* PES testing vacuum chamber.

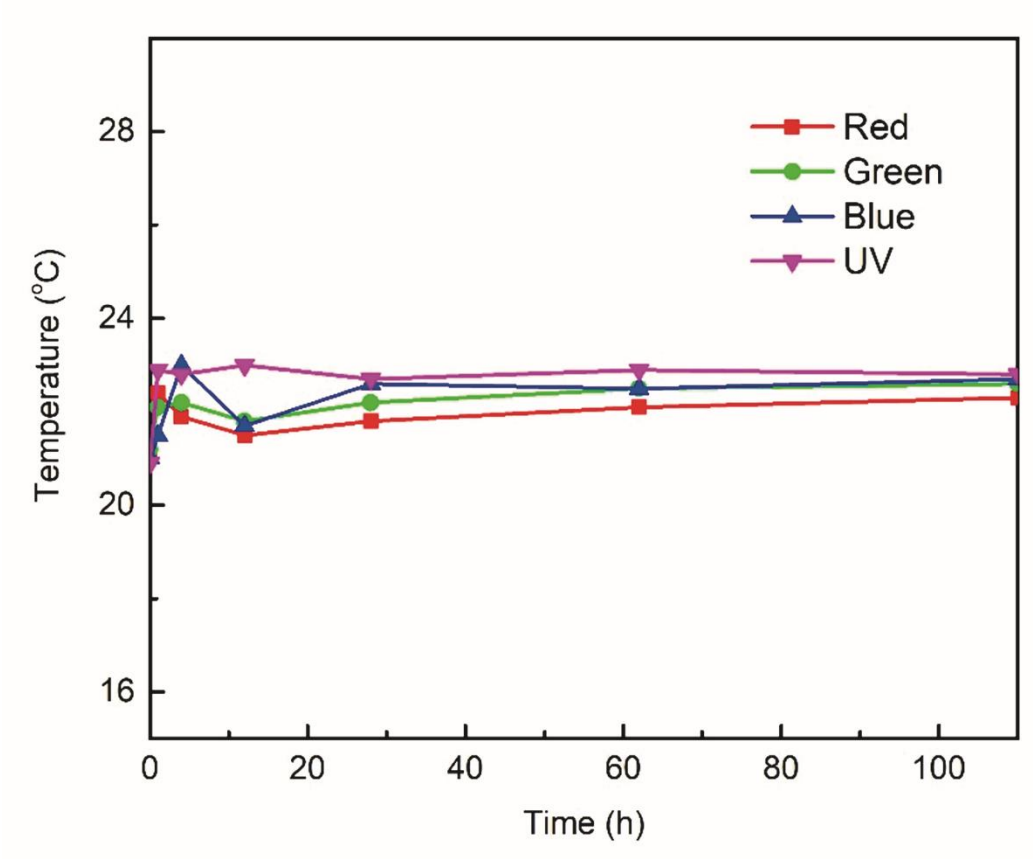

Figure S2. The variations of the sample temperature under continuous light illumination of red, green, blue and UV, which were measured by the model K digital thermometer.

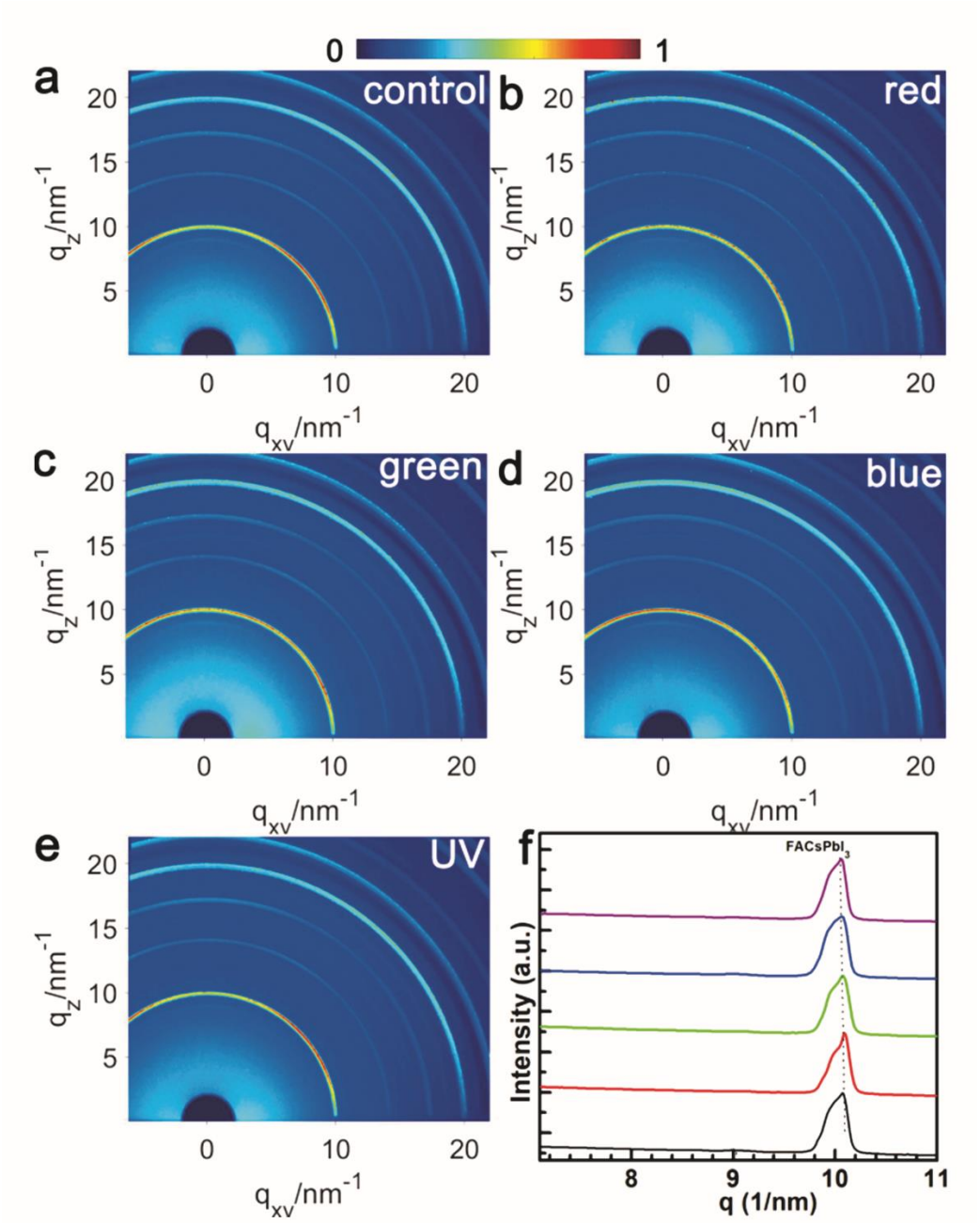

Figure S3. GIXRD patterns of α-$FACsPbI_3$ films under various light illuminations with an incidence angle of 0.5°. (a) Pristine perovskite film. (b-e) The samples were illuminated under (b) red, (c) green, (d) blue and (e) UV lights for 110 h, respectively. (f) Integration lines from 2D GIXRD patterns.

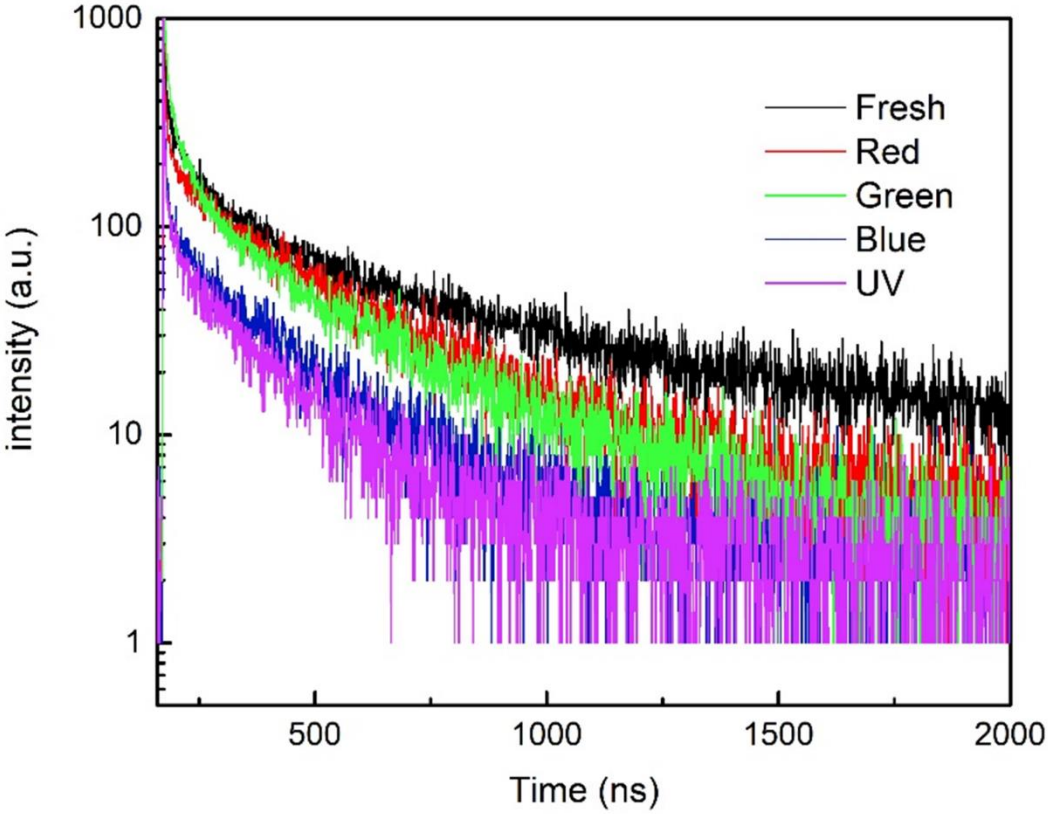

Figure S4. Time-resolved PL decay curves of perovskite samples under red, green, blue and UV illuminations for 110 h.

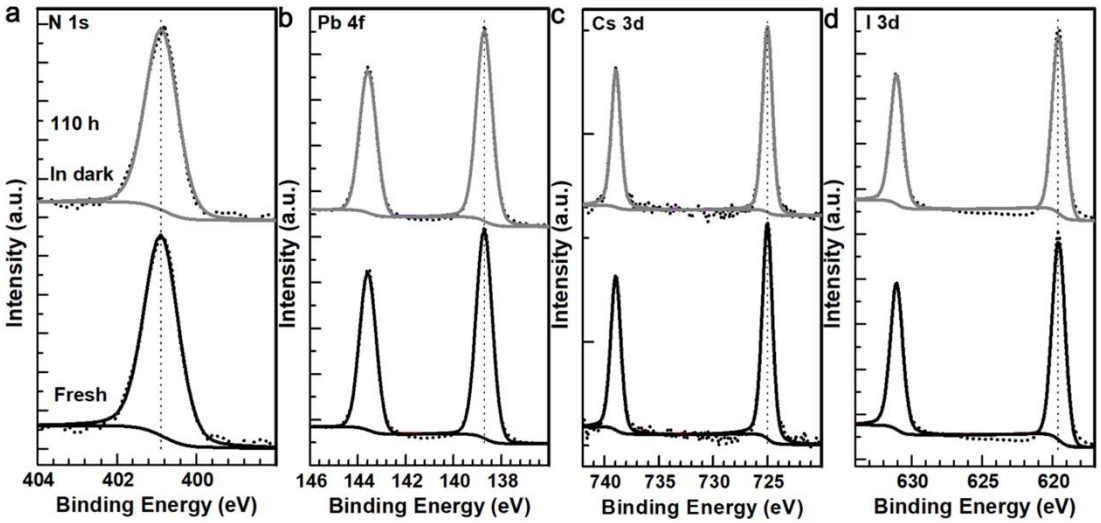

Figure S5. XPS spectra of (a) N 1s, (b) Pb 4f, (c) Cs 3d, and (d) I 3d core levels for the pristine α-$FACsPbI_3$ perovskites (black lines) and the samples stored in the dark UHV chamber for 110 h (gray lines).

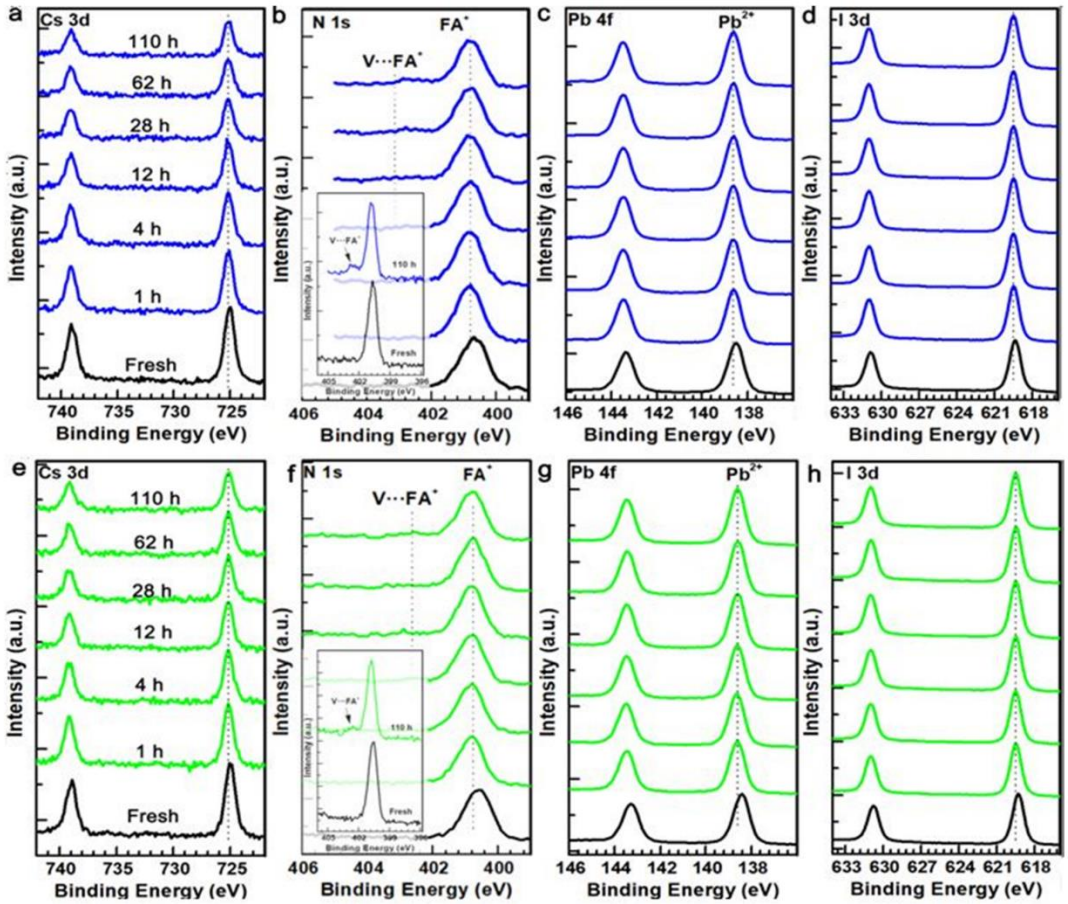

Figure S6. The evolution of XPS spectra of (a,e) N 1s, (b,f) Pb 4f, (c,g) Cs 3d, and (d,h) I 3d core levels in α-$FACsPbI_3$ perovskites as a function of illumination time. The pristine perovskites (black line) were characterized under illumination with light sources of blue light (blue lines) and green light (green lines).

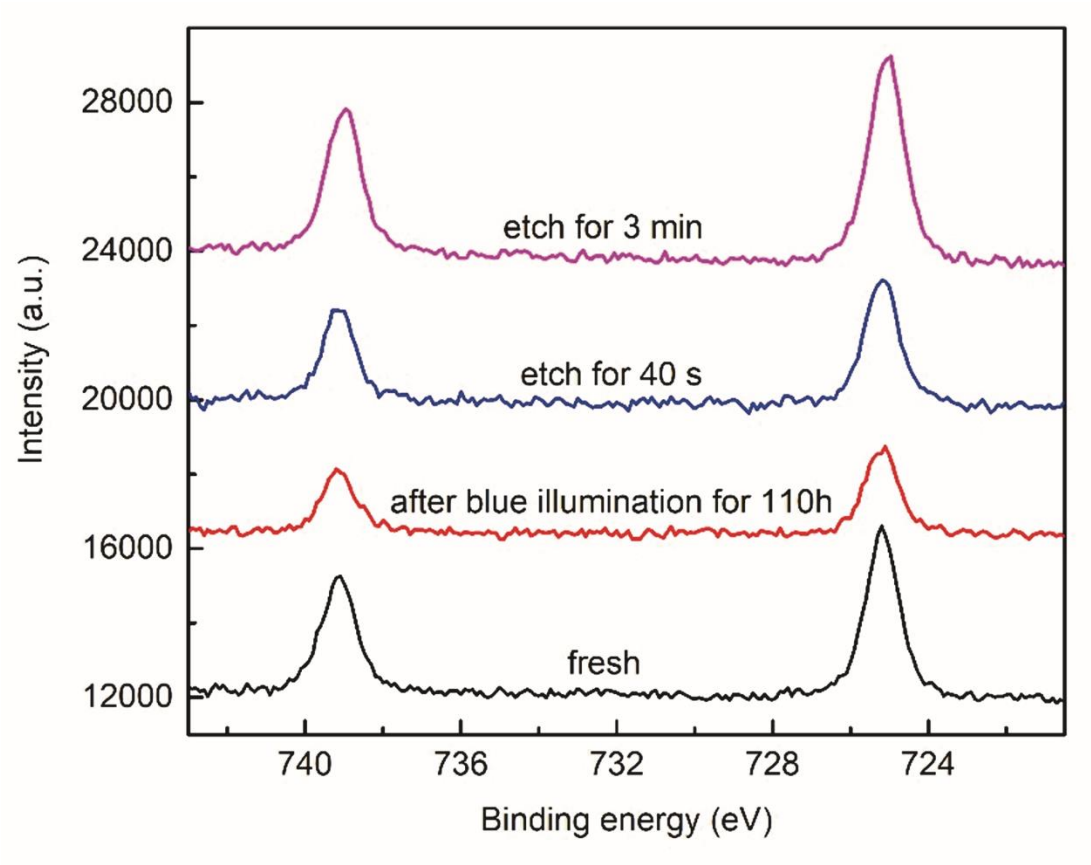

Figure S7. XPS depth characterization of the sample with the continuous Argon ion etching.

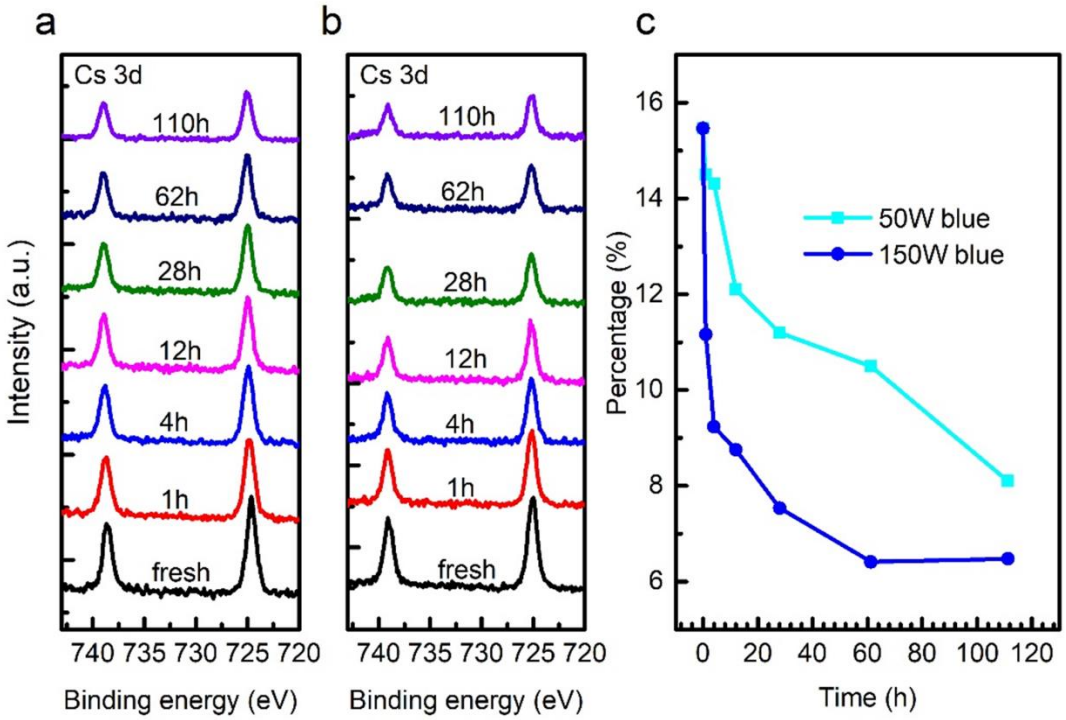

Figure S8. Light-induced Cs^+ migration under blue light with different intensity. XPS spectra of the Cs 3d core level under UV illumination with an intensity of (a) 50 W and (b) 150 W, respectively. (c) The variation of the Cs:Pb ratio as a function of illumination time.

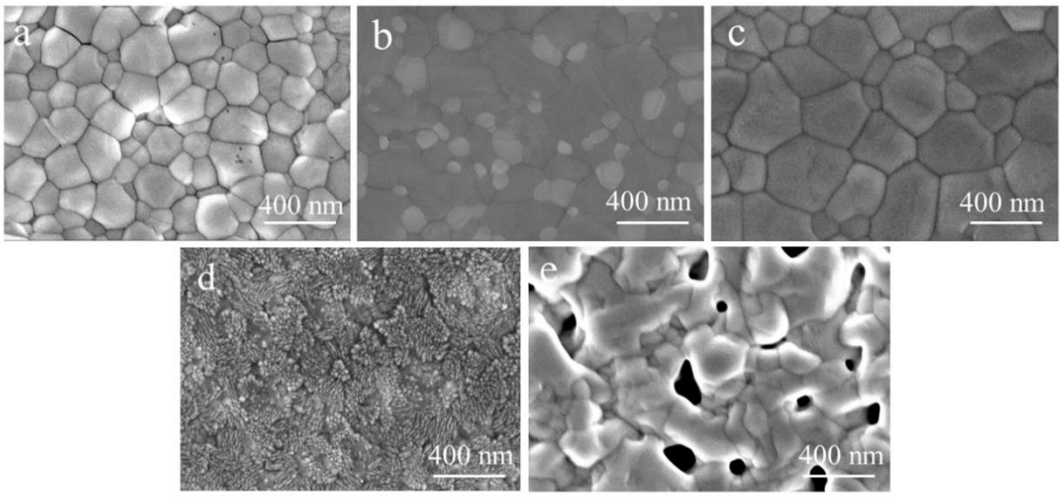

Figure S9. SEM images of the perovskite films with different phases. (a) α-$FACsPbI_3$, (b) α-$FAPbI_3$, (c) α-$CsPbI_3$, (d) δ-$FAPbI_3$ and (e) δ-$CsPbI_3$.