

## Supplementary Materials

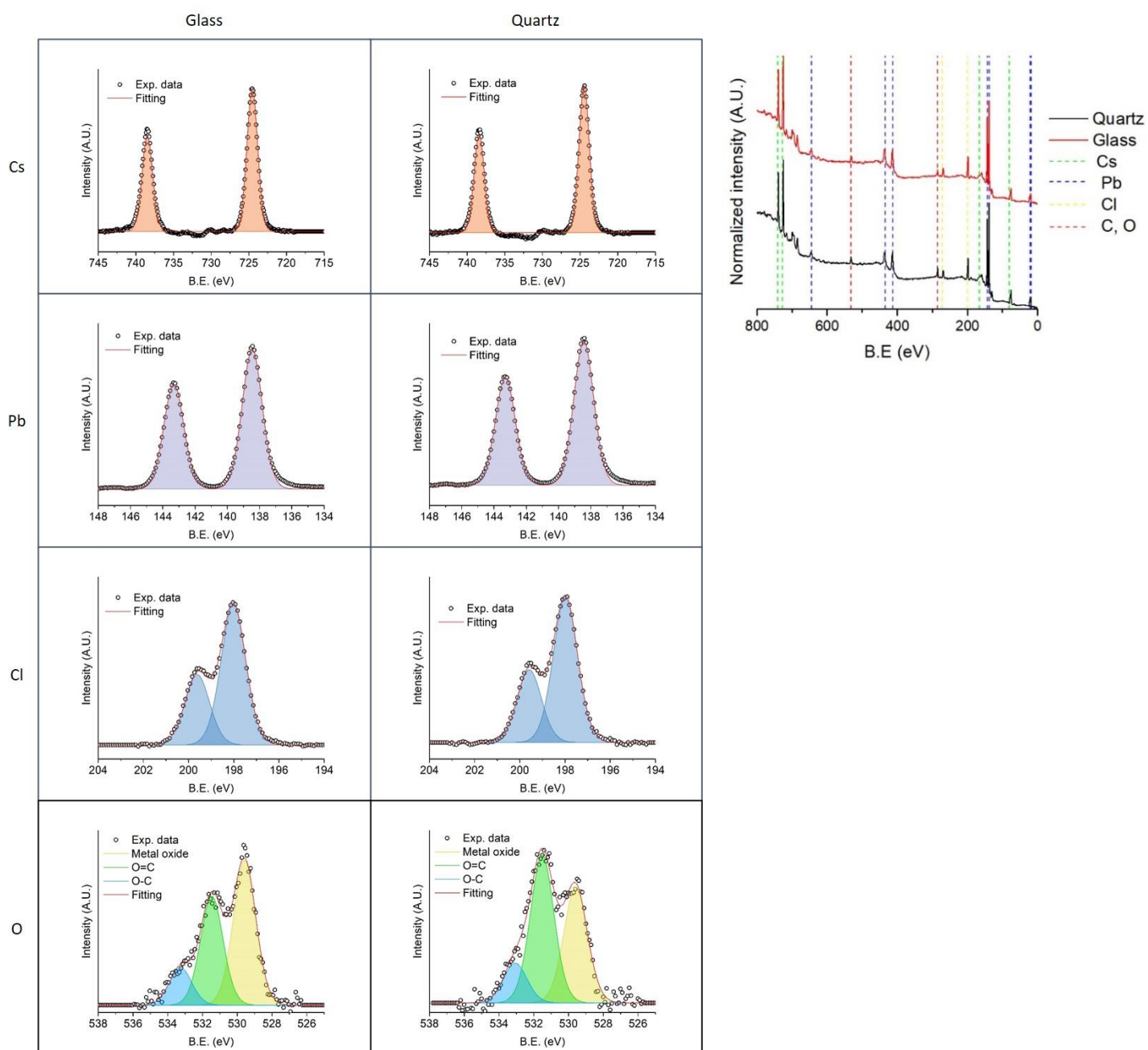
### Large-Area Nanocrystalline Caesium Lead Chloride Thin Films: A Focus on the Exciton Recombination Dynamics

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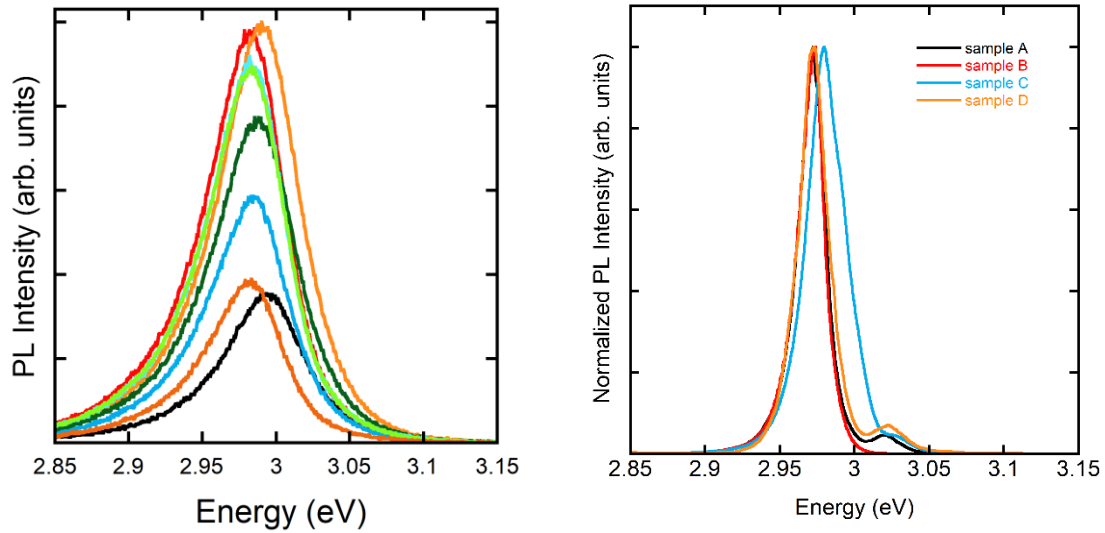
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Scanning electron microscopy (Philips XL30 SFEG SEM 30KV) and atomic force microscopy (Veeco Innova AFM, tapping mode scans with ultrasharp tips - radius of curvature of 2 nm) were performed to assess the morphology of the samples.

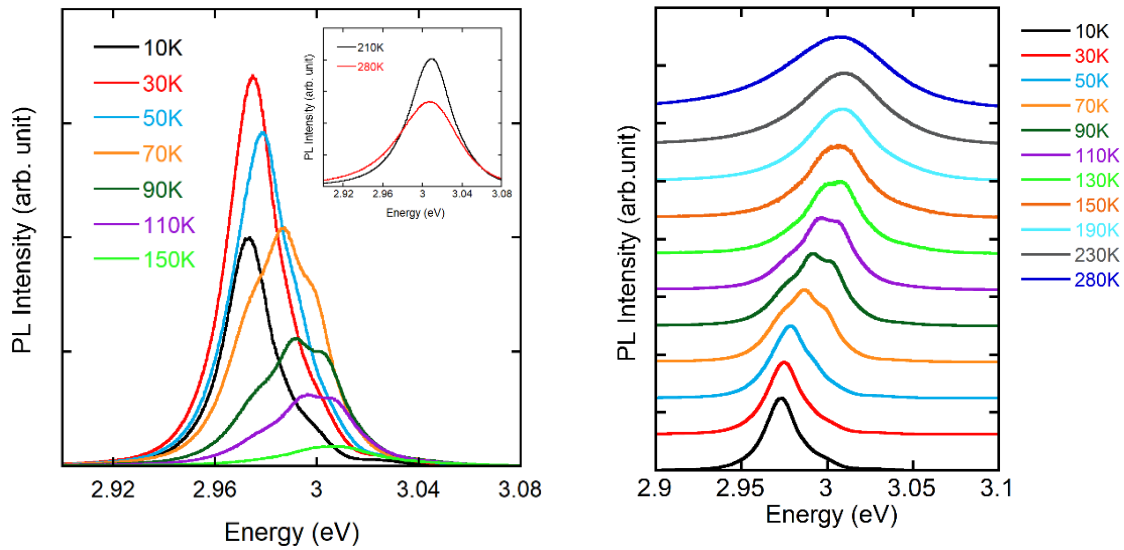
The chemical composition of the sample surface was determined using X-ray photoelectron spectroscopy (XPS) with an X-ray source (VSW Scientific Instrument Limited model TA10, Mg  $K\alpha$  radiation, 1253.6 eV) and a hemispherical analyzer (VSW Scientific Instrument Limited model HA100) with a 16 channels detector. To acquire the survey scan, the pass energy was fixed at 44 eV, for the high-definition spectra at 22 eV. The peaks were fitted using CasaXPS software and the background was subtracted using the Shirley's method [D. A. Shirley, Phys. Rev. B 1972, 5, 4709]. The binding energies values were calibrated using as internal reference the 1s transition of adventitious carbon fixed to 284.8 eV [P. Swift, Surf. Interface Anal. (1982) 4, 47].



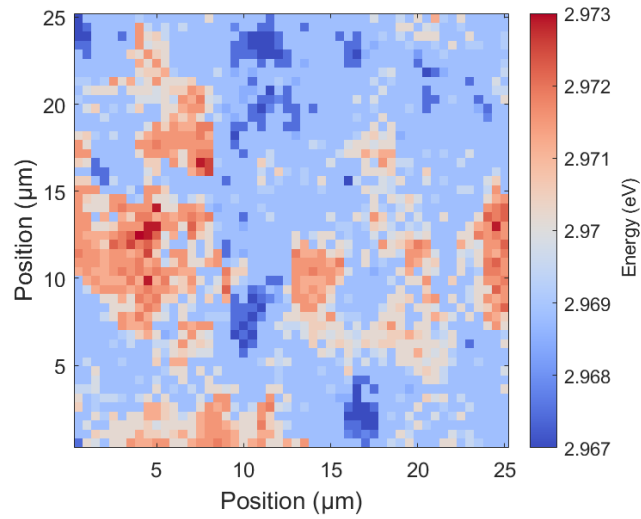
**Figure S1.** Left) XPS spectra of C and D samples, showing caesium (Cs), lead (Pb), chlorine (Cl) and oxygen (O) peaks; Right) Extended XPS spectra of the two samples. BE: Binding Energy.



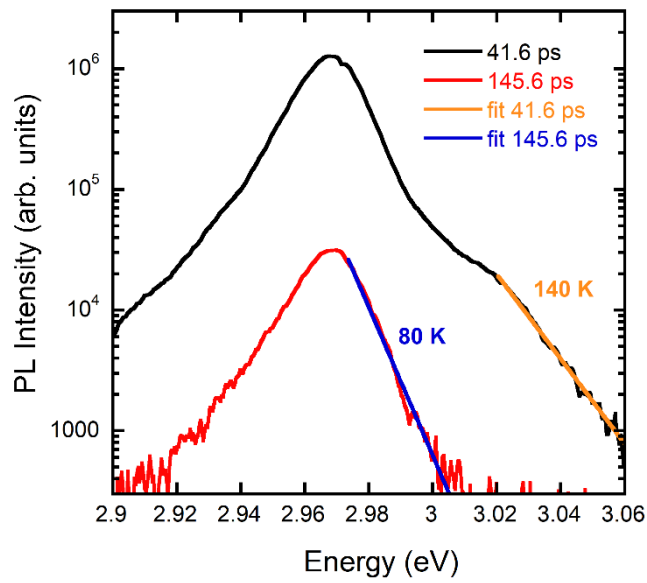
**Figure S2.** Left) Macro-PL spectra at room temperature in different spots of sample A, spanning an area of  $\sim 10$  cm<sup>2</sup>. Right) Macro-PL spectra of all samples at nominal 10 K. The shift of sample C respect to the other samples can be due to a different strain between the film and the substrate coming from a sample higher effective T (50 K).



**Figure S3.** Left) Macro-PL spectra of sample A as a function of temperature showing the PL quenching. In the insert the high temperature spectra are shown. Right) Vertically shifted macro-PL spectra of sample A as a function of temperature showing the peak energy shift.



**Figure S4.** Micro-PL map reporting the variation of the  $P_\alpha$  peak energy value in the same sample area of Figure 4 (main text).



**Figure S5.** Time resolved spectra of sample A showing the exponential thermal tail at two different time delays.