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Using Cathodoluminescence from Continuous and Pulsed-Mode SEM to Elucidate the Nanostructure of Hybrid Halide Perovskite Materials

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Hybrid halide perovskites are promising candidates for next-generation optoelectronic applications. They show heterogeneity at multiple lengthscales in their structural, chemical and optoelectronic properties [1]. Characterization techniques capable of revealing the structure-property relations are key to further understand this family of new materials.

Cathodoluminescence (CL) in a scanning electron microscope (SEM) is an excellent candidate for the investigation of semiconductor materials at the micro- and nano- scale. By scanning an electron beam over a semiconductor and collecting the optoelectronic properties of the material at sub-micrometre spatial resolution, CL-SEM can access the relevant lengthscales to understand structure-property relations of halide perovskites. While CL studies on inorganic halide perovskites are numerous, the characterization of hybrid (organic-inorganic) halide perovskites, including the highest-performing compositions, is limited due to their lower stability under the electron beam, namely beam damage.

In order to reduce beam damage (seen as an intermediate higher energy broader peak than the pristine perovskite emission), we used a state-of-the-art pulsed-beam (PM) CL-SEM to study hybrid perovskite compositions. The use of bright picosecond electron pulses in SEM not only enabled the acquisition of time-resolved CL but also reduced beam damage [2]. When PM was used, the CL spectra strongly resembled that of pristine perovskite emission, in which the perovskite emission was the dominating peak (see Figure 1). These findings suggest the use of PM for more robust high spatial resolution spectral mapping of beam-sensitive hybrid halide perovskite materials.

In this presentation, we showcase the advantages of using a PM electron beam for CL of beam-sensitive hybrid halide perovskites. We present a series of examples whereby CL from a PM and a low-current continuous wave mode (CW) electron beam aided in the study of luminescence of several different perovskite compositions. A first case study presented consists on understanding the effect that focused ion beam (FIB) milling had on the perovskite emission, generally considered to be a rough processing step for TEM specimen preparation. Using CL-SEM in PM, the perovskite layer in the lamellae was found to remain optically active, yet with a small blue-shift due to surface amorphization (Figure 2a) [3]. A second study presented consists on using CL to characterize state-of-the-art hybrid perovskite LEDs. By adding an organic additive to the perovskite LED precursor, film morphology could be manipulated and non-radiative losses suppressed. CL confirmed a reduction in non-radiative recombination in the perovskite grains and a higher homogeneity in the emission distribution in the sub-micrometer scale (Figure 2b).

All CL maps were acquired in an Attolight Allalin 4027 Chronos SEM-CL at room temperature under high vacuum. Beam focusing before each data acquisition was always performed away from the sample areas used for the measurements, to prevent specimen damage. CL maps were acquired using 3-10 kV acceleration voltage, low beam currents below 1 nA. The hyperspectral maps were processed and analyzed using the open-source Python package called LumiSpy [4]. A series of different hybrid halide perovskite compositions were used to prepare films on glass and to fabricate photovoltaic and LED devices. For photovoltaic device studies, the triple-cation double-halide composition $(FA_{0.8}MA_{0.15}Cs_{0.05})Pb(I_{0.8\text{-}0.9}Br_{0.1\text{-}0.2})_3$ was chosen, while for LEDs the $FAPbI_3$ composition was used (FA, formamidinium; MA, methylammonium).

In short, CL has proven to be extremely useful as a tool for the sub-micrometer optoelectronic properties characterization of hybrid halide perovskites. The findings presented here would not have been conceivable with the conventional high-current CL setups used to characterize traditional semiconductors due to limitations from beam damage. By carefully controlling electron beam dosage, CL starts to play a role in not only resolving the complex heterogeneity of the materials in the family of hybrid perovskites, but could also be key in understanding the properties and degradation of many other novel beam sensitive “soft” semiconductors [5].

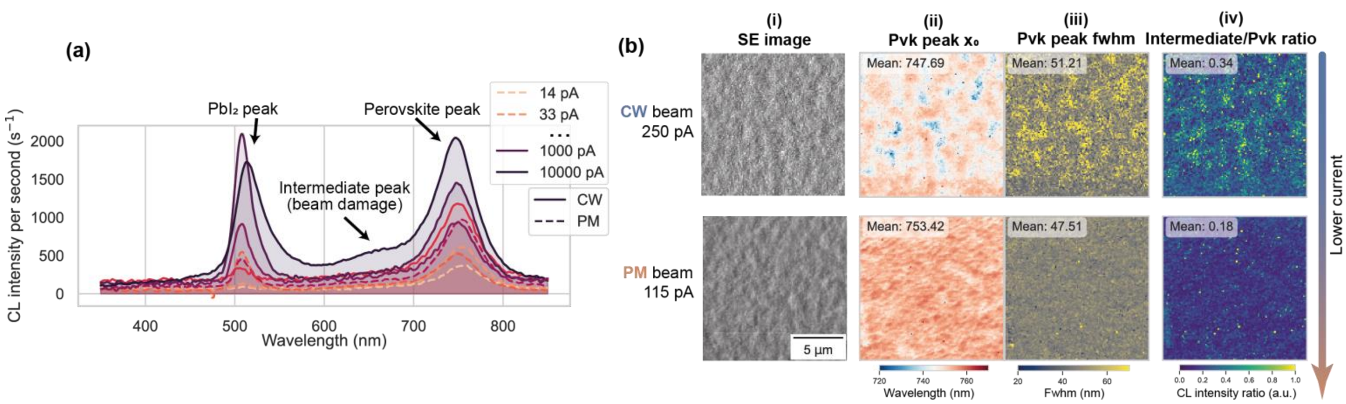

Figure 1. a) Spatially averaged CL spectra taken in CW and in PM (solid and dashed line) at varying beam currents. Three main peaks are observed, the intermediate peak linked to beam damage. b) SE image and CL map under low-current conditions. A Gaussian was fitted to each emission peak, with (i-iii) showing the fitted parameters for the perovskite phase and (iv) for the intermediate degradation phase to perovskite CL intensity ratio, an indirect measure of beam damage.

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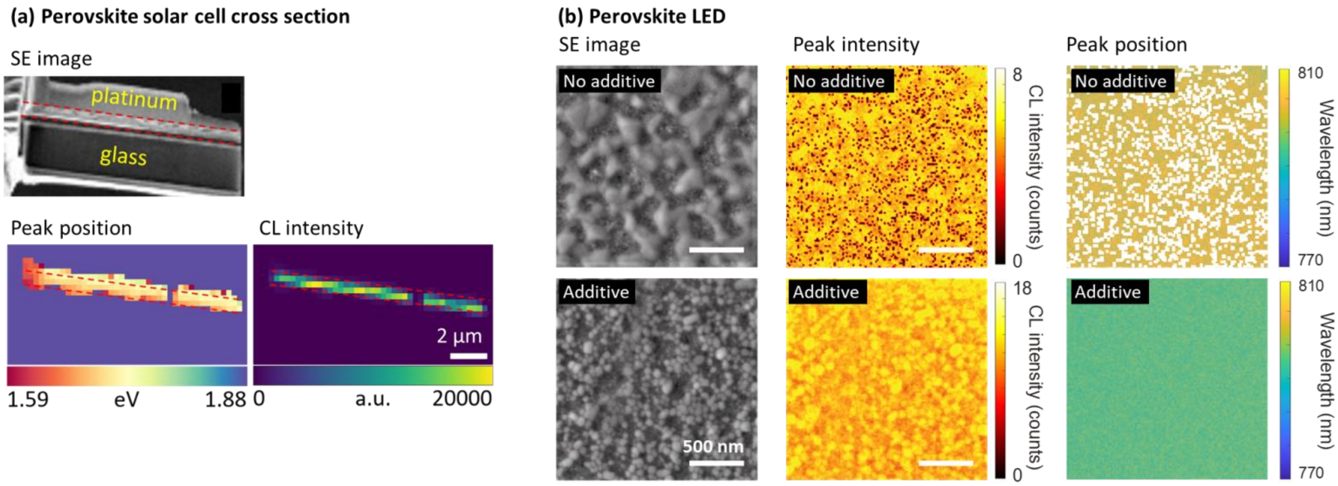

Figure 2. a) SE image and hyperspectral maps for the perovskite peak emission of a FIB-prepared hybrid perovskite lamellae showing the peak position and the CL intensity: the lamellae is still showing luminescence. b) SE images and CL hyperspectral maps for the $FAPbI_3$ peak in the LED samples without/with organic additive showing the peak intensity and emission peak homogeneity.

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