

## **Decoding the Complexity of Perovskite Photoluminescence: The Interplay of Defects, Their Dynamics, and Nanostructure**

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When discussing the properties of semiconductors, we usually focus on carrier and defect concentrations. In conventional semiconductor theory, knowing these concentrations is assumed to be sufficient to explain and predict material properties. For metal halide perovskite (MHP) thin films, however, this approach often falls short in explaining experimental observations. At least two peculiar features challenge this paradigm: the presence of pronounced defect dynamics[1,2] and the inherently nanostructured nature of these materials.[3–5]

In this talk, I will present results obtained using our photoluminescence (PL) microscopy setup, which enables PL imaging with micrometer-scale spatial resolution as well as time-resolved PL measurements under variable laser excitation and temperature. Several years ago, we developed a semi-automatic experimental protocol in which the photoluminescence quantum yield (PLQY) is measured as a function of laser repetition rate ( $R$ ) and pulse fluence ( $F$ ), producing a PLQY( $R,F$ ) map — a so-called “horse plot”. [2,6] These measurements are complemented by time-resolved PL decay kinetics recorded at different pulse fluences on the same sample. The resulting combined data set is exceptionally rich, making it a stringent benchmark for theoretical models, which must reproduce all observables simultaneously.[6] In addition, we developed a multi-pulse time-resolved PL technique in which excitation by bursts of short laser pulses provides straightforward access to different material states in terms of the populations of free and trapped charge carriers.[7]

I will argue that treating metal halide perovskite semiconductors as homogeneous in both space and time—the standard assumption in semiconductor theory—is often inadequate. My hypothesis is that many apparent properties of these materials do not arise from exotic physical mechanisms, but rather from neglecting ensemble and time-averaging effects that are intrinsic to most experimental techniques.

Most perovskite samples are nanostructured systems. As a result, charge-carrier dynamics are frequently governed by only a few discrete charge carriers and defect states within a relevant material volume, such as a single film grain or another structural domain. This leads to so-called “digitized” regimes, in which conventional continuous semiconductor models no longer directly apply.[8] A straightforward manifestation of this behavior is photoluminescence blinking observed in individual grains or crystals, caused by the activation and deactivation of individual non-radiative recombination centers that are present in very small numbers within the relevant volume.[5] In such cases, defect concentrations are no longer the appropriate descriptors; instead, integer numbers and stochastic models must be used in place of differential equations defined for continuous concentrations. Moreover, under illumination conditions relevant for applications, even electrons and holes themselves may need to be described in terms of discrete numbers rather than concentrations. This is because light is a flux of individual photons, each of which either generates an electron–hole pair or does not, and the average number of electron–hole pairs per crystal can easily approach or drop below unity.

These effects have a profound impact on photoluminescence dynamics and collectively lead to a substantial enhancement of the PLQY in nanostructured samples compared to bulk materials with the same average defect concentrations under identical illumination conditions. For example, in grains with dimensions of approximately  $50 \times 50 \times 100 \text{ nm}^3$ , photon-related “digitization” effects can increase the PLQY by several tens of percent even under 1-Sun illumination. Under low-intensity, room-light conditions, the resulting PLQY enhancement can be an order of magnitude larger than that predicted for a bulk sample. Importantly, these size-dependent effects are entirely unrelated to quantum confinement; instead, they arise solely from the corpuscular nature of light and from treating defects as discrete, individual entities.

Thus, crystal size—well beyond the quantum confinement regime—plays a crucial role in determining the PLQY, highlighting the importance of spatial structure on length scales of approximately 50–200 nm in luminescent materials and, most likely, in solar cells as well.

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