Mapping Structure-Property Relationships in Halide Perovskites with Correlated Nonlinear Ultrafast Microscopy

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The advancement of improved photoactive materials requires a deep understanding of their correlated spatial, spectral, and temporal properties. In principle, correlated time-resolved microscopy techniques can capture such information. Here, we illustrate how scanning electron microscopy (SEM) correlated to transient absorption microscopy (TAM) may be used to correlate heterogeneities in thin films of 2D and 3D perovskites with their optical properties. Statistical analysis of thousands of distinct spatial locations reveals the effects of grain boundaries and crystal size on carrier energetics and dynamics. In parallel to our measurement efforts, we have developed a high-throughput synthesis approach to enable discovery of new perovskite materials. Specifically, we have identified and characterized a new class of 2D perovskite by exploiting alloying of their organic cation. We show that the relatively large cation, ethylammonium (EA) may enter the cage of a 2D halide perovskite, causing distortions in the inorganic lattice such as Pb-I bond stretching. Spectroscopic and theoretical studies show that such structural deformation leads to a blue-shifted bandgap, sub-bandgap trap states with wider energetic distribution, and stronger photoluminescence quenching. These results and methods provide new insights for understanding the structure-property relationship in organic-inorganic photo-materials.

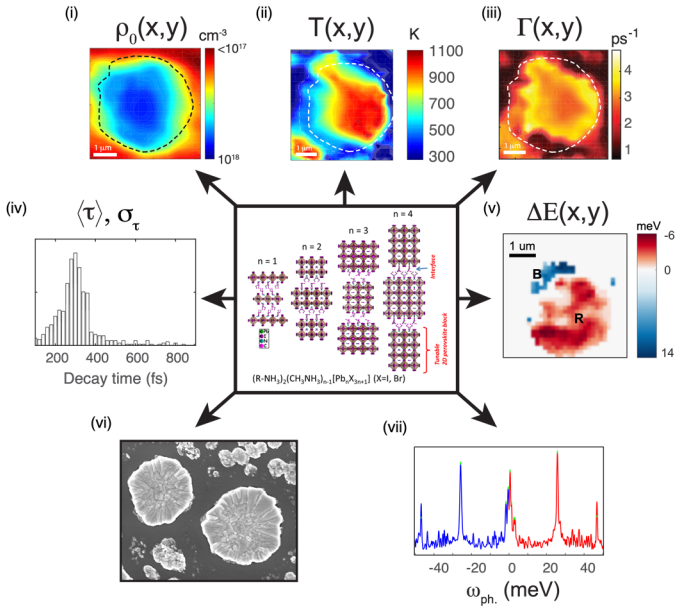

Figure 1. Correlated optical- and scanning probe microscopies are used to map heterogeneities in 2D and 3D perovskite materials. When combined with statistical analysis, direct correlations between structure-property-dynamics may be established.

1. Jiang, X., Jun, S., Hoffman, J., Kanatzidis, M.G., Harel, E., Global Analysis for Time and Spectrally Resolved Multi-Dimensional Microscopy: Application to CH3NH3PbI3 Perovskite Thin Films, *J. Phys. Chem.* **2020**, 124, 4837-4847
2. Li, X., Fu, Y., Pedesseau, P., Guo, P., Cuthriell, S., Hadar, I., Even, J., Katan, C., Stoumpos, C.C., Schaller, R.D., Harel, E, Kanatzidis, M.G., Negative Pressure Engineering with Large Cage Cation in 2D Halide Perovskite Causes Lattice Softening, *J. Am. Chem. Soc.* **2020**, 142, 11486-11496
3. Fu, Y., Jiang, X., Li, X., Traore B., Spanopoulos J, Katan, C., Even, J., Katan, C., Kanatzidis, M.G., Harel, E, Cation Engineering in Two-Dimensional Ruddlesden-Popper Lead Iodide Perovskites with Mixed Large A-Site Cations in the Cage, *J. Am. Chem. Soc.* **2020**, 142, 4008-4021