Ultrafast nano-imaging of polaron dynamics in lead halide perovskites

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Abstract: To investigate the spatio-temporal heterogeneity in the ultrafast soft-lattice and polaron dynamics of lead halide perovskites, we develop ultrafast heterodyne-detected infrared nano-imaging resolving nanoscale disorder in polaron formation, coupling, and dynamics.

1. Introduction

Hybrid organic-inorganic perovskites exhibit extraordinary photovoltaic performance, which is believed to arise from almost liquid-like low-energy interactions among lattice ions and charge carriers. Specifically, the dynamic lattice plays a central role in stabilizing photoinduced carriers by forming polarons, where lattice phonons "dress" electrons and holes. Unlike conventional photovoltaics, perovskite films exhibit spatial variations in their optoelectronic responses over multiple length scales. However, there has been a critical missing link between the observed optoelectronic non-uniformity and the underlying heterogeneity in the carrier-phonon coupling.

We have recently addressed this outstanding problem using spatio-spectral infrared vibrational nano-imaging. In femtosecond nano-FTIR infrared scattering scanning near-field optical microscopy (IR *s*-SNOM), we observed heterogeneous cation-lattice coupling and associated vibrational dynamics in a spin-coated film of a formamidinium (FA)-methylammonium (MA)-cesium triple cation perovskite (Fig. 1) [1]. Such structural and dynamical disorder suggested heterogeneous charge-phonon coupling when photoinduced electrons and holes were injected.

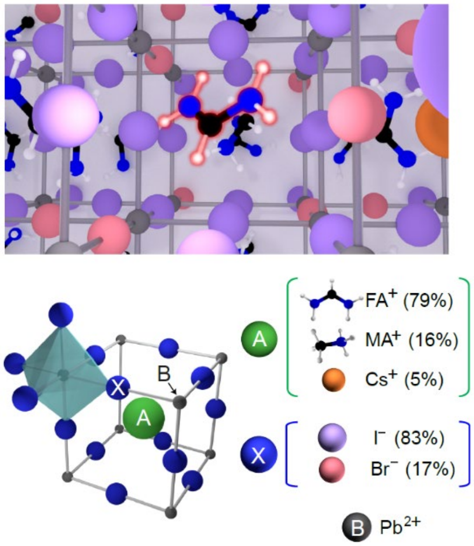

Fig. 1. Three-dimensional structure and chemical composition of FAMACs triple cation perovskite.

Here, we report the development of ultrafast heterodyne-detected infrared nano-imaging and -spectroscopy with spatio-temporal-spectral resolution. In its application to triple cation perovskites, we resolve nanoscale heterogeneity of polaron formation, its picosecond relaxation dynamics, and the nanolocalized transient vibrational signature of the polaron-cation coupling. This provides a real time and real space view of photoexcitation and polaron dynamics as the key elementary photophysical process underlying perovskite solar cell performance.

2. Ultrafast Heterodyne-Detected Infrared Nano-Imaging and -Spectroscopy

From quantum materials to energy materials, the ultrafast evolution of low-energy responses and interactions defines their unique properties and functionalities, often with characteristic spatial heterogeneity at the nanoscale. However, access to the complex interplay among the spatial variations, time-dependent dynamics, and energy-scale of the low-energy processes has remained elusive. We have previously demonstrated ultrafast pump-probe nano-spectroscopy with amplified laser pulses for far-from equilibrium excitation, with time and space resolution [2]. Building on this work, we have now developed heterodyne-detected ultrafast infrared nano-spectroscopy with spatio-temporal-spectral resolution [3]. Here we directly characterize a time-domain profile of a pump-probe signal field by interferometric optical heterodyne detection with high sensitivity. The spectral resolution allows for the complete characterization of the transient optical response function on the nanoscale, as well as at femtosecond time scale.

Fig. 2A and 2B show the schematic and conceptual illustration of the experimental setup. The visible pump pulse (516 nm) and mid-infrared probe pulse (tunable from 5 – 10 μm) are collinearly focused onto the apex of a metallic tip in an atomic force microscope (AFM) operating in tapping mode. These two pulses together induce a third-order polarization, which sources the nano-localized pump-probe signal. The emitted signal field is interfered with another reference pulse, through which we directly characterize the time-domain profile of the pump-probe signal field. We selectively and sensitively characterize the pump-probe signal of near-field origin by detecting the signal component modulated both by the AFM tapping frequency and pump modulation frequency.

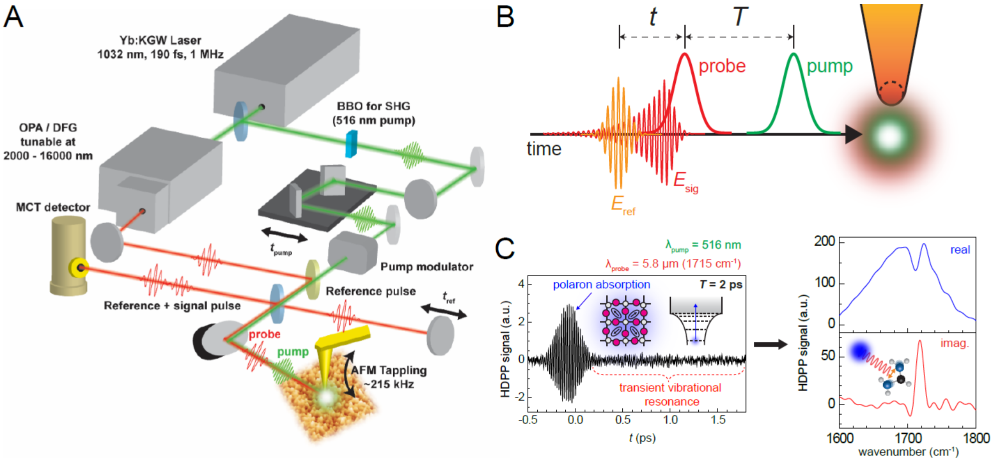

Fig. 2. **A.** Schematic illustration of heterodyne-detected pump-probe infrared nano-imaging system. **B.** The timing scheme for the experiment. The third-order nano-localized polarization emits a signal field, which we characterize directly in time domain. **C.** Interferometrically detected transient vibrational signal observed in time and frequency domains, arising from polaron-cation coupling.

3. Polaron-Cation Coupling at the Nanoscale – Transient Vibrational Nano-Spectroscopy

Ultrafast vibrational spectroscopy has been successful in elucidating dynamic evolutions of molecular interactions in a variety of condensed phase systems, ranging from biological to material systems. One of the molecular cations in the perovskite, formamidinium (FA), exhibits a strong vibrational resonance arising from the CN anti-symmetric stretch mode [1]. Upon the injection of photoinduced carriers, the surrounding inorganic lattice and organic cations, including FA, dynamically reconfigure their structures and orientations to stabilize the carriers, forming polarons. This coupling between molecular cation and polaron enhances the vibrational transition dipole moment of the FA cation, and also induces a blue-shift in the molecular vibrational frequency.

To observe this transient vibrational resonance as a signature of polaron-molecular coupling, we apply ultrafast heterodyne-detected infrared nano-spectroscopy to a triple cation perovskite. A visible pump pulse at 516 nm injects polarons into the film, followed by readout with a mid-infrared probe pulse that is tuned to be spectrally resonant with the CN anti-symmetric stretch mode of the FA cation. In the time-domain pump-probe interferogram, we clearly observe a center burst followed by a long-lasting coherence. While the center burst arises from a broadband polaron response, the long-lasting coherence represents the transient vibrational resonance. Upon a Fourier transform of this interferogram, we observe a distinct peak arising from the transient vibrational resonance. The transient vibrational resonance appears as an enhanced absorptive peak that is blue-shifted from the ground state, signifying polaron-cation coupling.

The detection of the transient vibrational resonance at fs-nm resolution allows us to infer the nanoscale heterogeneity in cation-polaron coupling, particularly in relation to the role of organic cations in forming polarons which is widely debated in the field of perovskite photophysics.

4. Heterogeneous polaron formation and dynamics

Further, when the infrared probe spectrum is tuned to ~1200 cm^{-1}, we observe a large near-field pump-probe signal, allowing us to map the heterodyne pump-probe signal amplitude and its time dependence, yielding a pump-probe nano-image (Fig. 3A-C) [4]. The strong pump-probe signal at ~1200 cm^{-1} has recently been attributed, in a far-field study, to polaron absorption based on its characteristic spectral line shape and unique temperature dependence [5]. Therefore, the observed spatial variation in the pump-probe signal amplitude and its time-dependence potentially reflects the non-uniformity in polaron formation and its relaxation dynamics.

The observed polaronic disorder directly links the low-energy charge-phonon interactions to the optoelectronic heterogeneity. Some domains and grains exhibit larger polaron population and/or longer lifetime, suggesting the presence of grains with superior photovoltaic performance. The optoelectronic performance of perovskites can thus be potentially further improved by controlling such nanoscale heterogeneity of polarons.

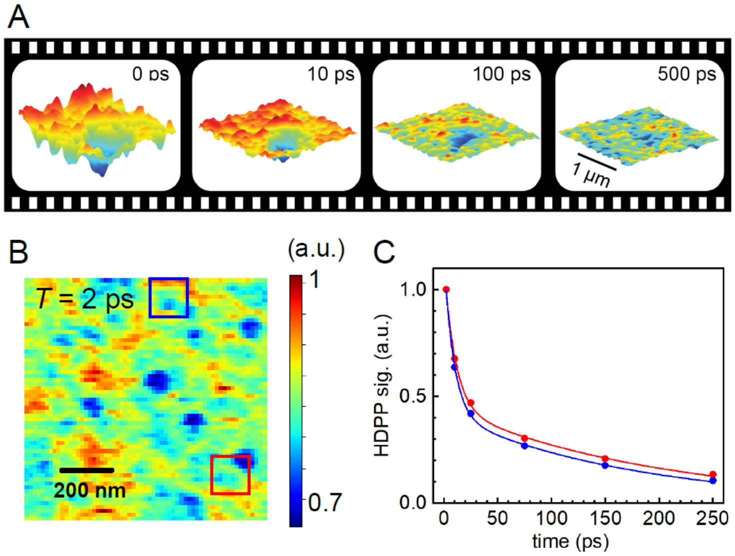

Fig. 3. **A.** The "polaron movie" acquired by heterodyne-detected visible-pump infrared-probe nano-imaging. **B.** The heterogeneity in the pump-probe signal at the early waiting time of 2 ps, reflecting non-uniformity in polaron formation. **C.** The decays in the pump-probe signal amplitude at the two different locations indicated by solid squares in B, demonstrating the spatial variation in polaron relaxation dynamics.

5. Conclusion

Using our newly developed heterodyne-detected near-field pump-probe nano-imaging and -spectroscopy, we resolve the nanoscale heterogeneity in the formation of polarons and their relaxation dynamics. Such polaronic disorder accounts for the optoelectronic heterogeneity in perovskites, which have been intensely studied in recent years. The understanding and control of polaronic disorder at the nanoscale are critical for further enhancement of the perovskite-based device performance.

6. References

[1] J. Nishida et al., "Heterogeneous cation-lattice interaction and dynamics in triple-cation perovskites revealed by infrared vibrational nanoscopy," *ACS Energy Lett.*, 5, 1636 (2020)

[2] S. A. Dönges et al., "Ultrafast Nanoimaging of the Photoinduced Phase Transition Dynamics in VO_2," *Nano. Lett.* 16, 3029 (2016)

[3] J. Nishida et al., in preparation.

[4] J. Nishida et al., in preparation.

[5] K. Munson et al., "Dynamic Disorder Dominates Delocalization, Transport, and Recombination in Halide Perovskites," *Chem.*, 4, 2826 (2018)