

Coherent and Dynamic Small Polaron Delocalization in CuFeO₂

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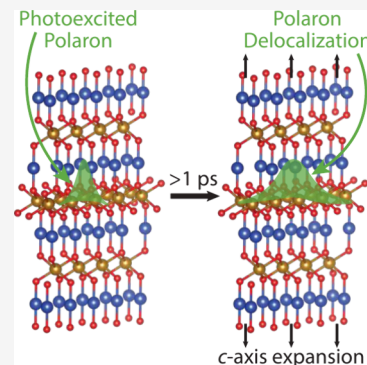


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ABSTRACT: Small polarons remain a bottleneck in realizing efficient transition metal oxide devices. Routes to engineer small polaron coupling to electronic states and lattice modes to control carrier localization remain unclear. Here, we measure small polaron formation in CuFeO₂ using transient extreme ultraviolet reflection spectroscopy and compare to theoretical predictions in realistically parametrized Holstein models, demonstrating that polaron localization depends on coupling to high-frequency versus low-frequency phonon bath components. We measure small polaron formation on a comparable ~ 100 fs timescale to other Fe(III) compounds. Dynamic delocalization of the polaron follows formation through a coherent lattice expansion between Fe–O layers and charge-sharing with surrounding Fe(IV) states. Simulations reveal two major factors dictate polaron formation timescales: phonon density and reorganization energy distributions between acoustic and optical modes, matching experimental findings. Our work shows how electronic-structural coupling in a polaron-host material can be leveraged to suppress polaronic effects for various applications.



Polarons play a significant role in various material physics, encompassing superconductivity, charge density waves, and electronic transport in both organic and inorganic materials.^{1–6} In transition metal oxides with narrow bandwidth, the interplay between strong electron correlations and strong electron–phonon coupling determines properties ranging from band structure to charge transport.⁶ For materials with photocatalytic applications, the effect on surface chemical kinetics that benefit from charge localization and lattice reorganization must also be considered.^{7,8} Iron oxide compounds, such as α -Fe₂O₃ (hematite), are prototypical photocatalysts that possess ideal charge-transfer-based band gaps in the visible spectrum and surface kinetics due to their localized d-orbitals. However, their efficiency falls short of the theoretical maximum because the same properties lead to the formation of photoexcited small polarons, which reduce carrier mobility.⁹ While transition metal oxides that have an empty d-shell after bonding, such as TiO₂, tend to form photoexcited large polarons with sufficient carrier mobilities to approach near-theoretical efficiencies, the same bonding also usually leads to large UV bandgaps that limit overall solar absorption efficiency.¹⁰

The dynamics of small polaron formation are well studied and understood, but the mechanism for delocalizing polarons to improve carrier lifetimes remains unclear.^{8,11} In α -Fe₂O₃, the photoexcited electron distorts the local lattice upon the initial electron–optical phonon scattering, forming small polarons that trap photoexcited carriers with a large carrier effective mass. One proposed approach to suppress small polaron formation is to introduce new atoms at the unit cell

level, thereby decreasing the reorganization energy of the small polaron below the thermal energy.¹² Understanding the effect of atomic substitutions on small polaron formation dynamics and their correlation to photoexcited charge transport is necessary for improving photocatalysis and engineering other small-polaron-based applications.

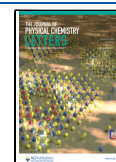
In this work, we measure the delocalization of small polarons in CuFeO₂ using transient extreme ultraviolet (XUV) spectroscopy and compare the formation dynamics directly to *ab initio* calculations, which consider coupling to both the optical and acoustic phonon bath. CuFeO₂ has a delafossite structure (Figure 1A) with 2D Cu atomic layers substituted between Fe–O networks and was identified by high-throughput screening techniques as a potential high-performing photocatalyst.^{13–15} XUV measurements of CuFeO₂ have demonstrated cathodic photocurrent not present in hematite in addition to suggestions of small polaron formation, which are further explored here.¹⁶ The Cu atoms are expected to modulate small polaron formation in two ways: by providing increased electronic screening between photoexcited polarons in the Fe–O layers and by allowing the lattice to expand perpendicular to the Fe–O plane to reduce reorganization

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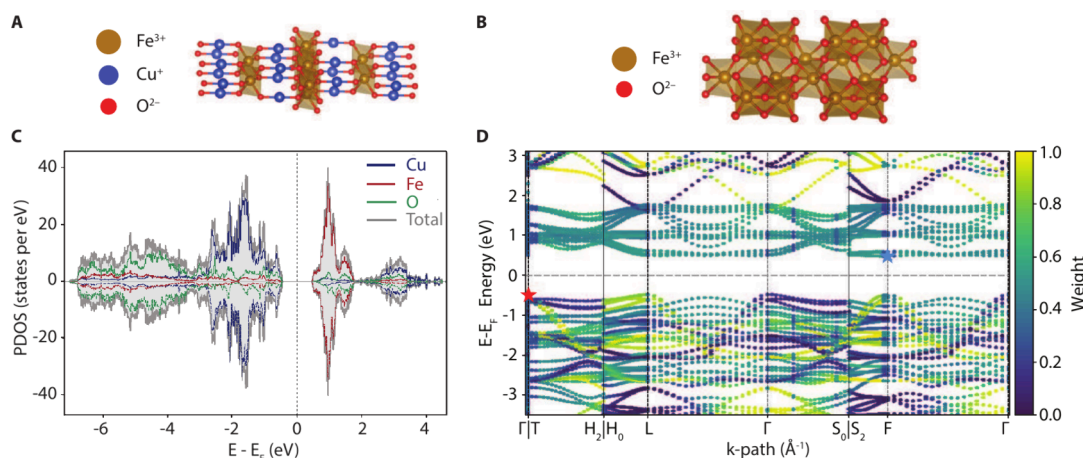


Figure 1. A comparison of the (A) delafossite crystal structure of CuFeO_2 where Cu atoms are inserted between Fe–O layers and (B) hematite ($\alpha\text{-Fe}_2\text{O}_3$). (C) The projected density of states shows that the conduction bands are dominated by Fe orbital character while the valence bands are mixed with Cu–O orbitals. (D) The band structure of CuFeO_2 , where red (blue) stars indicate the VBM (CBM). The weights indicate the extent to which each supercell Bloch state contributes to the corresponding primitive cell state.

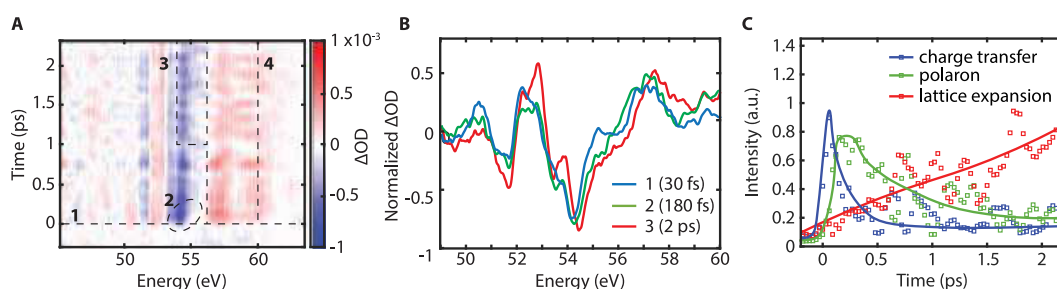


Figure 2. Transient XUV reflection–absorption spectrum of CuFeO_2 (A) following photoexcitation with a 400 nm pump. The red and blue colors represent increased and decreased absorption after photoexcitation, respectively. Four main spectral features are labeled in the plot. At pump–probe overlap (t_0), a series of positive and negative peaks are observed (label 1). Immediately after photoexcitation, an ultrafast spectral blue shift is observed around 55 eV (label 2), which is attributed to octahedra expansion and small polaron formation. At longer pump–probe time delays, spectral intensity and energy oscillations are observed (label 3), which is attributed to polaron induced coherent acoustic phonons. At higher XUV transition energies, increased XUV absorption is observed and attributed to photoinduced Fe(IV) states (label 4). Experimental lineouts (B) at 30 fs (blue), 180 fs (red), and 2.04 ps (green) which correspond to dynamics in label 1, label 2, and label 3, respectively. (C) Kinetics plot of the charge transfer (blue), polaron (green), and lattice expansion (red) states with “best fit” lines to visualize the kinetics of the chosen dynamics while disregarding the coherent phonon oscillations.

potentials. Our transient XUV measurements indicate that electronic screening between layers does not change the small polaron formation rate from the standard <100 fs measured for most Fe(III) oxides.^{11,17,18} Quantum dynamics simulations demonstrate that this polaron formation timescale depends on electronic-structural coupling to different frequency components of the phonon bath. The ability of the lattice to expand perpendicular to the Fe–O plane is measured to enable a polaron delocalization on a picosecond timescale through a coherent Cu–(Fe–O) c -axis phonon mode.¹⁹ A corresponding nearest-neighbor Fe(III) to Fe(IV) charge compensation supports the hypothesis of an initial small-electron-polaron delocalizing beyond the initial Fe(III) site to the nearest neighbors.²⁰ Transient absorption microscopy reveals that the delocalized polaron leads to a longer recombination timescale when compared to $\alpha\text{-Fe}_2\text{O}_3$ with similar crystallinity conditions.^{17,21–23} Beyond photocatalysis, the results provide insight into a broad range of small-polaron-based materials and how lattice interactions and electron correlations can be leveraged to tune their properties.

Figure 1A shows the crystal structure of CuFeO_2 , where the Fe–O sublattices are capped by Cu layers along the c -axis. $\alpha\text{-Fe}_2\text{O}_3$

is a prototypical example of photoexcited small polaron formation at an Fe(III) site and is shown in Figure 1B for reference.^{8,17} CuFeO_2 is a charge transfer insulator (Figure 1C) similar to $\alpha\text{-Fe}_2\text{O}_3$, in which the valence band maximum (VBM) is dominated by Cu–O hybridization and the conduction band minimum (CBM) is dominated by Fe 3d orbitals. The additional electron density offered by the Cu atoms in the CuFeO_2 provides hybridization between the Cu and O atoms, which reduces the material’s band gap compared to $\alpha\text{-Fe}_2\text{O}_3$ and increases valence band dispersion (Figure 1D). The conduction bands are still relatively flat despite the delocalization offered by the Cu atoms, suggesting that localized electronic states persist in the Fe–O sublattice despite the addition of Cu.

Transient XUV spectroscopy is used to measure small polaron formation dynamics in thin film CuFeO_2 following a 3.1 eV (400 nm) photoexcitation of the charge transfer transition from the Cu–O orbitals to Fe 3d orbitals. The optical excitation fluence was $\sim 6 \text{ mJ/cm}^2$, which results in an initial photoexcited carrier density of $\sim 4.4 \times 10^{21} \text{ cm}^{-3}$.^{24–26} The XUV pulse is generated from few-cycle broadband white light with energy centered around the Fe $M_{2,3}$ edge at $\sim 54 \text{ eV}$.

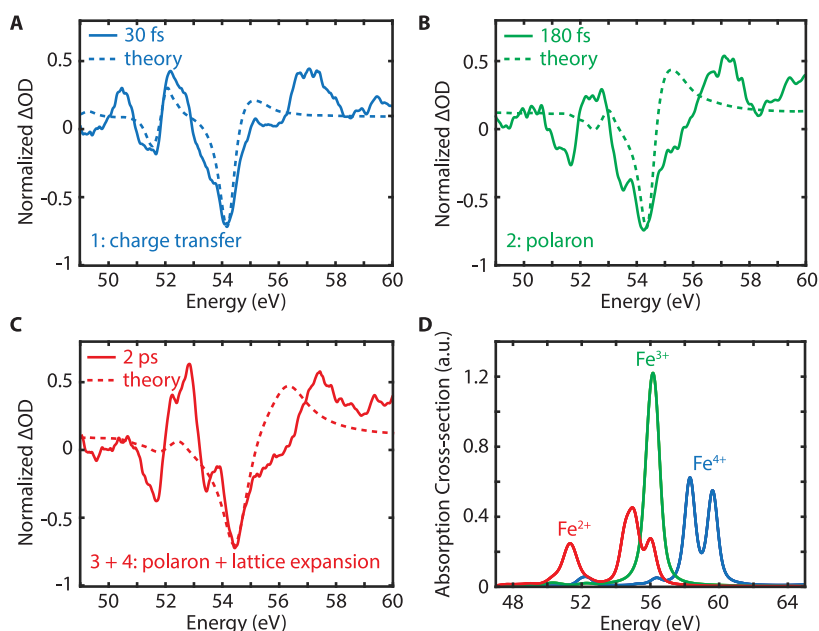


Figure 3. Experimental lineouts (solid lines) compared to BSE theory (dashed lines) for immediately after photoexcitation (A), following polaron formation (B), and the change to the polaron spectrum following lattice expansion (C), which correspond the label 1, label 2, and labels 3 and 4 in Figure 2A, respectively. Ligand-field theory (D) for differing oxidation states of iron. The blue trace corresponding to Fe(IV) appears at the same energy as Figure 2A, label 4.

Transient XUV reflection spectroscopy is performed at a 10° grazing incidence angle, resulting in a penetration depth estimated as ~ 2 nm.²⁷ After photoexcitation, the change in the

XUV spectrum is defined as $\Delta OD = -\log_{10} \left(\frac{I_{\text{pump on}}}{I_{\text{pump off}}} \right)$. The

definition is often termed reflection–absorption due to the negative sign. Under this convention, the increase in spectral intensity (red color) in Figure 2A is roughly associated with increased absorption, whereas the blue color is roughly associated with decreased absorption. Additional experimental details, including characterization of the CuFeO₂ sample, can be found in the Supporting Information.

The measured transient XUV spectrum for the Fe $M_{2,3}$ edge is shown in Figure 2. Four distinct spectral features are identified (Figure 2A). Immediately following photoexcitation, a series of positive and negative spectral features occur between 51 and 56 eV (Figure 2A, label 1). This is followed by a fast spectral blue shift around 55 eV within the first ~ 100 fs (Figure 2A, label 2). There are intensity oscillations in the measured spectra at longer time delays. A clear intensity oscillation is observed for the main negative peak at ~ 55 eV. An increased oscillation in spectral density occurs between 55.5 and 56.6 eV, which is out-of-phase compared to the oscillation of the main negative peak between 54.5 and 55.5 eV (Figure 2A, label 3). In addition to the features between 51 and 56 eV, there are two major absorption peaks above 56 eV. These peaks emerge immediately after photoexcitation and exhibit oscillating spectral features that strongly correlate with spectral intensities below 56 eV and are out-of-phase with the oscillations between 54.5 and 55.5 eV. It should be noted that while the features in labels 1 and 2 are common among transient XUV measurements of α -Fe₂O₃ and other prototypical Fe(III) small polaron materials,^{8,11,28,29} the features in labels 3 and 4 are not typically observed in the transient XUV spectra of photoexcited iron oxides. This suggests that the

interstitial Cu layer between the Fe–O octahedra influences longer timescale dynamics.

The observed spectral changes are dominated by changes to the angular momentum coupling X-ray transition Hamiltonian at the Fe $M_{2,3}$ edge, so the measured spectra relate more to oxidation states and local bonding rather than state-filling of photoexcited carriers.³⁰ To understand the spectral features, we simulate the transient XUV reflection spectra of CuFeO₂ using a previously verified adiabatic approximation to an *ab initio* excited state Bethe–Salpeter equation (BSE) treatment of the XUV spectra (Supporting Information). Figure 3A–C compares experimental spectral lineouts taken from 30 fs after photoexcitation to 2 ps after photoexcitation (Figure 3A–C) with BSE theory. The lineout immediately following photoexcitation at 30 fs matches a modeled photoexcited charge transfer state (Figure 3A). In contrast, the lineout at 180 fs agrees with a modeled small polaron state (Figure 3B). Kinetically, the small polaron forms in 90 ± 20 fs, consistent with previous measurements of Fe(III) oxides.^{17,18} The theoretically predicted changes match for both lineouts in terms of the shift of the zero crossing and the appearance of a new multiplet peak at 54.5 eV.

The spectral features in labels 3 and 4 in Figure 2A are where the dynamics of CuFeO₂ differ from previously measured iron oxide materials. The spectral splitting seen in Figure 2A, label 3 matches theory for a *c*-axis lattice expansion in the DFT unit cell starting around one picosecond after the small polaron has formed (Figure 3C). When the small polaron is formed, the oxygen octahedra around the new Fe(II) site expand locally due to the quench of the Fe–O bond strength. This secondary lattice expansion around the polaron site expands the bond length between the oxygen and nearest neighboring Fe(IV) sites through a *c*-axis expansion, delocalizing the polaron wave function from its initial state. The lattice expansion correlates with coherent phonon oscillations measured within this region. Specifically, intensity

modulation occurs between 55.4 and 56.4 eV, oscillating out of phase compared to the intensity between 54.5 and 55.2 eV (Figure 2A, labels 3 and 4). The intensity oscillations of the differential spectra between 55.4–56.4 eV is plotted in Figure 4A. Initial oscillations are damped due to the optical phonons

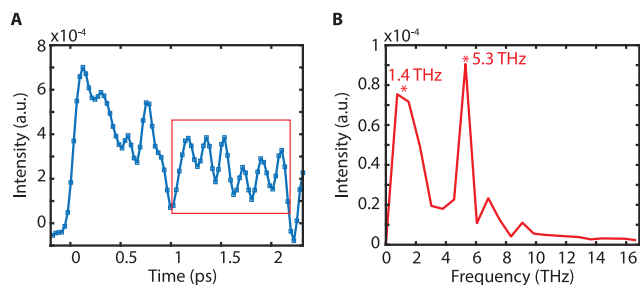


Figure 4. Spectral oscillations (A) in the main negative feature at ~ 55 eV in Figure 2A label 3. The oscillations in the red box were Fourier transformed (B) and demonstrate Cu–(Fe–O) c -axis acoustic modes at 1.4 THz and a mixture of Fe–O modes at 5.3 THz.

associated with small polaron formation, but after ~ 1 ps, a Fourier analysis reveals that dominant oscillations at 1.4 and 5.3 THz are present (Figure 4B). These frequencies correspond to mixed acoustic and optical Cu–(Fe–O plane) modes along the c -axis and along Fe–O bond lengths, respectively.¹⁹ Due to the large anisotropy of the CuFeO₂ lattice, phonon modes polarized along the c -axis are much softer and anharmonic than those along the ab -plane, enabling a low-frequency c -axis lattice expansion that coherently couples to localized polaron-induced octahedra expansion.

The spectral features at energies above 56 eV (Figure 2A, label 4) are well represented by the formation of a local Fe(IV) state immediately after photoexcitation which would agree with a delocalization of the Fe(II) small-polaron state through lattice expansion. Modeling local oxidation states in the BSE calculations is challenging, given that carriers are filled up to the photoexcited energy in the adiabatic perturbation limit. To understand oxidation state effects, a ligand-field theory calculation using CTM4XAS is performed and reinforces that the increased XUV absorption above 56 eV is due to Fe(IV) absorption (Figure 3D).³¹ This feature also has oscillations that are out-of-phase with the Fe–O and Cu–O bond motions seen in the negative spectral features at 1.4 and 5.3 THz and plotted in Figure 4A–B. The intrinsic oxidation state in CuFeO₂ in the ground state is Fe(III); our measurement suggests that there is a sudden increase in Fe(IV) states after the photoexcited charge transfer transition. This state then oscillates out-of-phase with the Fe–O and Cu c -axis lattice

motions, coupling to the polaronic state and dynamically delocalizing it.

The kinetics for each spectral feature are shown in Figure 2C. The Fe(IV) state in the nearest-neighbor shell forms immediately after the Fe(III) to Fe(II) charge transfer transition from photoexcitation. However, the polaron delocalization through the oscillation between the ground state bleach and Fe(IV) states does not occur until an order of magnitude longer ~ 1 ps timescale, compared to the ~ 100 fs small polaron formation measured here and in other Fe(III) oxide systems.^{17,18} The transient XUV data confirm that Cu-hybridization does not alter the small polaron formation energy or kinetics through electronic screening, but rather reduces the on-site reorganization energy, which ultimately delocalizes the small polaron. The small polaron formation and delocalization process are shown schematically in Figure 5 for CuFeO₂. Comparatively, in α -Fe₂O₃, the charge transfer initiated by photoexcitation induces a small electron polaronic state, resulting in lattice distortion and carrier trapping until recombination. In CuFeO₂, charge transfer also induces small polaron formation; however, the nearest neighboring atoms compensate for this charge transfer by becoming Fe(IV) in character. The lattice expansion then allows for polaron delocalization on a picosecond timescale.

To theoretically investigate small polaron formation and its associated kinetics, we employ the dispersive Holstein Hamiltonian,³² which encodes the coupling between electronic excitations and local phonons. We parametrize this model using experimental measurements³³ (i.e., Raman spectra) and electronic structure calculations of the materials of interest^{34–37} (see Supporting Information). We describe coupling to phonon modes via a continuous spectral density, $J(\omega)$, which we model using two Lorentzians centered on clusters of Raman-active modes around 545 and 1100 cm^{−1}. Figure 6A shows six peaks taken from the experimental Raman spectrum of CuFeO₂ and the resulting bimodal spectral density.³⁸ We further note that, consistent with spectral densities parametrized from molecular dynamics simulations in other materials, one expects the coupling distributions to low-frequency phonons to be broad and high-frequency phonon modes to be narrow.^{39–42} In CuFeO₂, the reorganization energy (λ) that quantifies the total exciton–phonon coupling significantly exceeds the exciton hopping integral (ν). This allows us to employ the perturbative Non-Interacting Blip Approximation (NIBA),⁴³ augmented with our recent generalized master equation framework to reach large system sizes free from finite-size effects,⁴⁴ to predict the quantum dynamics of the polaron, and enabling us to quantify the

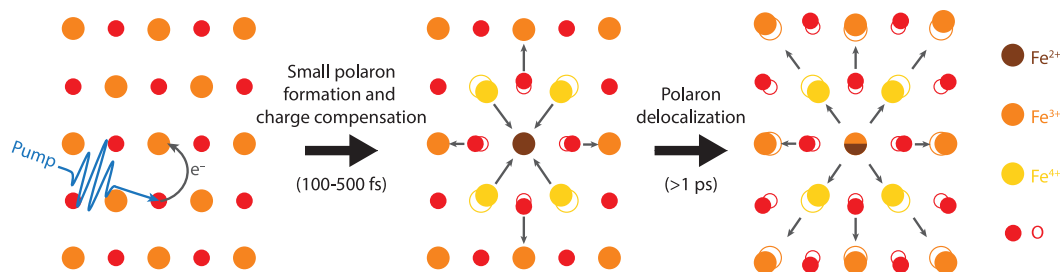


Figure 5. Schematic representation of the polaron formation mechanism in CuFeO₂. The formation of Fe⁴⁺ states around polaron sites and the expansion of the lattice enables delocalization of polarons on a ps timescale.

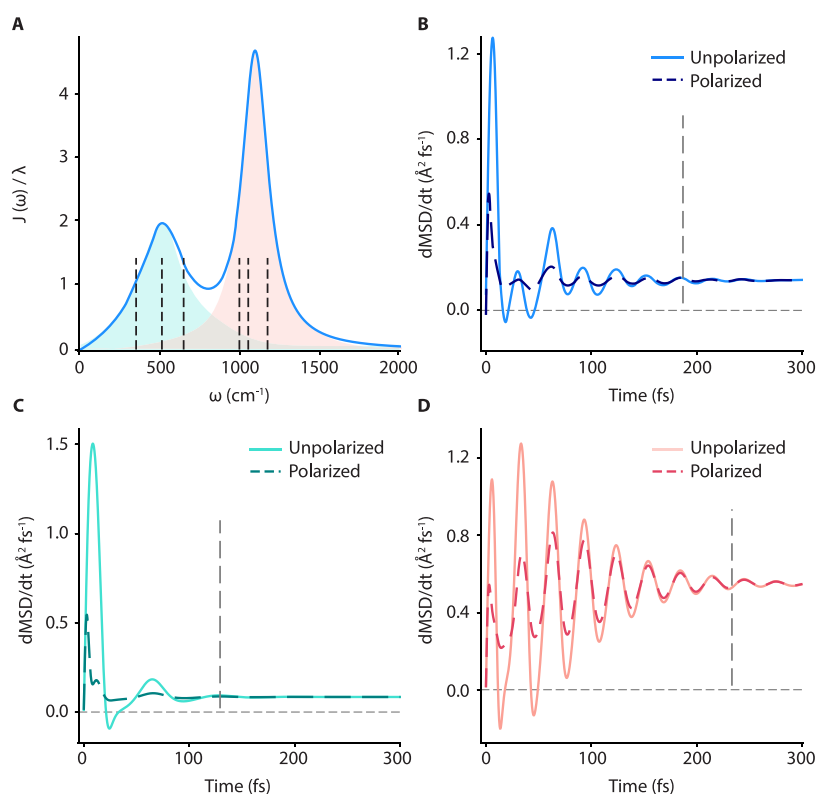


Figure 6. Tunability of Holstein polaron formation times via the exciton–phonon coupling distributions. (A) Bimodal Lorentzian spectral density based on Raman-detected phonon modes (gray dashed lines). The green and red shaded regions correspond to the low- and high-frequency regions of the full spectral density, respectively. (B)–(D) Polaron formation times for exciton–phonon couplings described by (B) the bimodal distribution in (A), (C) the low-frequency contribution of the bimodal distribution in (A) with the full reorganization energy, and (D) the high-frequency contribution of the bimodal distribution in (A) with the full reorganization energy. (B)–(D) show the derivative of the polaron’s mean squared displacement, $dMSD/dt$, for both *polarized* and *unpolarized* nonequilibrium initial conditions. Gray dashed lines indicate the polaron formation times (i.e., when both nonequilibrium simulations start to agree).

influence of phonon timescales on the speed of polaron formation.

Because polaron formation timescales are not a direct observable from the quantum dynamics, we extract them indirectly.⁴⁵ Since the lattice relaxation of polaron formation is a nonequilibrium effect, the time required for the dynamics to become independent of the initial nonequilibrium preparation of the electronic excitation quantifies the polaron formation time. We employ two distinct nonequilibrium preparations of the initial excitation: one where the bare exciton arises from an impulsive Franck–Condon excitation (unpolarized) and is subsequently allowed to move and one where we allow a static exciton to fully polarize its lattice before it is allowed to move (polarized). We track the deviation between the derivatives of their mean squared displacement (MSD), which encodes polaron mobility, and when these derivatives agree, the polarons have shed their global nonequilibrium preparation, signaling the completion of their local lattice relaxation. We identify the duration of this nonequilibrium relaxation as the polaron formation time.⁴⁵

To understand how the form of the spectral density affects the polaron formation time, and therefore how to engineer exciton–phonon couplings to control these, we perform a detailed numerical study (see the [Supporting Information](#) section VII). In addition to our earlier insight that increased exciton–nuclear coupling decreases polaron formation times,⁴⁵ we also observe that polaron formation becomes faster when coupled to a *wide and continuous* distribution of phonon

frequencies. Further, for a given coupling, these timescales are modulated by the distribution of reorganization energy between the optical and acoustic modes, with increasing weight in the narrow, high-frequency optical modes slowing down polaron formation. Surprisingly, the rate of formation was insensitive to the (mean) vibrational frequency.

For the spectral density appropriate to CuFeO₂, there is a competition of factors, with the larger, high-frequency phonon couplings also having a narrow distribution. Computationally, we unpack the spectral density to understand the relative importance of the low- and high-frequency regions. Keeping the reorganization energy fixed, when considering only the broadly distributed slow (low-frequency) phonons, the timescale of polaron formation is ~ 130 fs ([Figure 6C](#)).⁴ Contrastingly, the narrowly distributed fast (high-frequency) phonons exhibit a much longer formation timescale of ~ 230 fs ([Figure 6D](#)). Together, the full $J(\omega)$ encompassing both regions ([Figure 6B](#)) gives a value of ~ 185 fs (which is a weighted combination of the above; see [Figure S17](#)). We therefore conclude that the addition of narrowly distributed, high-frequency optical phonon modes increases the polaron formation times. Since it is a general feature of condensed phase systems for low-frequency phonon couplings to exhibit spectrally dense, quasi-continuous distributions while couplings to high-frequency phonons are narrowly spectrally distributed, these results are likely applicable beyond transition metal oxides.

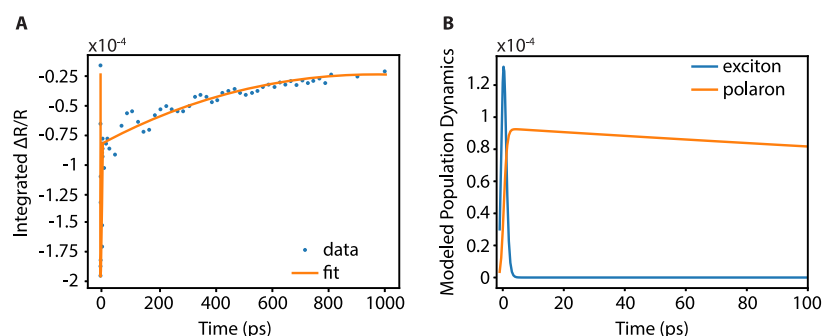


Figure 7. Optical reflectivity of CuFeO₂ (A) and extracted lifetimes of the charge transfer state and polaron state (B). An 8 GHz acoustic phonon oscillation is observed at longer times in the spectra.

We further conclude that broadly distributed, low-frequency modes dissipate energy faster and more smoothly than narrowly distributed, high-frequency modes (see the [Supporting Information](#) section VII). The smoother response and shorter timescale for low-energy acoustic phonon coupling indicate that the multipicosecond rise of polaron delocalization in [Figure 2C](#) likely represents the growing occupation of the acoustic phonon bath as the polaron couples to a lattice expansion.

The intersection of experimental and theoretical results also has substantial implications for the description of small polaron physics in transition metal oxides. In particular, the experiment further suggests that, after the polaron is formed, acoustic modes are populated, both in response to the polaron formation and due to the decay of high-energy optical phonons. However, the Holstein model, which offers the standard description of small polaron formation in these materials,^{46–48} cannot account for such hierarchical energy flow among phonon modes. Instead, the Holstein model offers a field theoretic description of nuclear fluctuations that subsumes energy transfer-facilitating anharmonicities into an effective Gaussian phonon bath. Hence, while Holstein descriptions of small polaron physics can yield useful insights and design principles as we have shown above, precise vibrational engineering further requires the ability to explicitly probe vibrational energy flow in the presence of anharmonic phonons.

Finally, we measure the role of the delocalized polaron state on the carrier lifetime. Interconversion between the polaron and charge transfer state is also examined and confirmed by a variant of optical transient reflectance spectroscopy.^{49,50} A pump beam of 540 nm center wavelength and ~ 0.5 ps duration is focused down to a spot with $1/e^2$ width of 270 nm on the sample to create above-bandgap excitations in the CFO. Subsequently, a wide-field 707 nm probe pulse of similar duration illuminates the sample. The probe reflection is collected by a CMOS camera, and its intensity is integrated over spatial coordinates. The transient reflectance signal is the difference between probe reflectance with and without the pump pulse, scaled by the pump-off reflectance:

$$\Delta R/R = \frac{I_{\text{pump on}} - I_{\text{pump off}}}{I_{\text{pump off}}}$$

In [Figure 7](#), signatures of both the polaron and charge transfer state have negative amplitude but with different strengths. At short timescales ($\sim$ ps), a very sharp drop is observed in the transient reflectance signal ([Figure 7A](#)), corresponding to the fast decay of the charge transfer state as it is converted to the lower amplitude polaron. This longer-lived

polaron signal persists for hundreds of ps. The entire kinetic trace is fitted with an instrument response function (0.7 ps) convolved with kinetic equation $Ae^{-kt} + B\frac{k}{k_p - k}[e^{-kt} - e^{-k_pt}]$, where A and B are relative amplitudes of the charge transfer and polaron states, respectively. The extracted lifetimes of the charge transfer state ($1/k$) and polaron ($1/k_p$) are 0.52 and 770 ps. The amplitudes of the charge transfer state and polaron have a ratio of 5.6:1. A low energy acoustic mode at 8 GHz also modulates the signal. Optical transient absorption spectroscopies have observed these low-energy GHz acoustic coherent phonons in other polaron-forming iron oxides and perovskites.^{51,52}

The measured kinetics using transient reflectance agree with the transient XUV findings. Given the temporal resolution of the instrument response function, an initial charge transfer state convolved with a localized polaron persists for picoseconds before transforming into the delocalized polaron state, which then persists on the order of a nanosecond. The finding is intriguing because, although the CuFeO₂ is polycrystalline with grain boundaries, it has a lifetime that persists several hundred picoseconds longer than hematite with similar crystallinity conditions.^{21–23} The delocalization of the polaron acts to mitigate carrier recombination and extend the lifetime of the localized carriers enabled by population of the acoustic phonon bath. This presents a parameter to tune when engineering polaron-forming semiconductors for photocatalysis, optoelectronics, and other applications.

The outcomes of this work provide new insight into small polaron-dominated materials and phenomena. We did not find that Cu atom hybridization changed the small polaron formation kinetics, most likely due to strong Fe–Fe electron correlations still dominating interactions. However, changing the lattice degrees of freedom was directly correlated with increasing the delocalization of the small polarons by lowering polaron reorganization energies. Leveraging simulations of lattice descriptions of small polarons in transition metal oxides, we further find that two major factors dictate polaron formation timescales: spectral phonon density and reorganization energy distributions between acoustic and optical modes. Specifically, we find that phonon bath engineering favoring strong coupling to broad acoustic phonon distributions in favor of narrowly distributed optical modes decreases polaron formation timescales. We further find that polaron delocalization is a dynamical process that occurs after the formation of small polarons, contrasting with the concept of immediate delocalized polaron formation.²⁸ Furthermore, the delocalization of the polaron appears to be related to longer

photoexcited lifetimes in the material when compared to prototypical hematite. This work provides insights into more mobile polarons in desirable transition metal oxides, as well insights into coherent control of the lattice response to small polaron formation.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.5c03430>.

CuFeO₂ synthesis and characterization, experimental methods, theoretical methods, spectral analysis, quantum dynamics simulations (PDF)

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Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTE

^aThe same distribution without scaling the reorganization energy has a slightly longer timescale of 140 fs; see Figure S19.

■ REFERENCES

(1) Mott, N. F. Polaron models of high-temperature superconductors. *J. Phys. Condens. Matter* **1993**, *5*, 3487–3506.

- (2) Zhang, L.; Chu, W.; Zhao, C.; Zheng, Q.; Prezhdo, O. V.; Zhao, J. Dynamics of photoexcited small polarons in transition-metal oxides. *J. Phys. Chem. Lett.* **2021**, *12*, 2191–2198.
- (3) Ghosh, R.; Spano, F. C. Excitons and polarons in organic materials. *Acc. Chem. Res.* **2020**, *53*, 2201–2211.
- (4) Kudinov, E. K. Model of a polaron superconductor. *Phys. Solid State* **2002**, *44*, 692–703.
- (5) Zhang, C.; Sous, J.; Reichman, D.; Berciu, M.; Millis, A.; Prokofev, N.; Svistunov, B. Bipolaronic high-temperature superconductivity. *Physical Review X* **2023**, *13*, No. 011010.
- (6) Nosarzewski, B.; Huang, E. W.; Dee, P. M.; Esterlis, I.; Moritz, B.; Kivelson, S. A.; Johnston, S.; Devereaux, T. P. Superconductivity, charge density waves, and bipolarons in the Holstein model. *Phys. Rev. B* **2021**, *103*, 235156.
- (7) Yim, C.; Watkins, M.; Wolf, M.; Pang, C.; Hermansson, K.; Thornton, G. Engineering polarons at a metal oxide surface. *Phys. Rev. Lett.* **2016**, *117*, 116402.
- (8) Biswas, S.; Wallentine, S.; Bandaranayake, S.; Baker, L. R. Controlling polaron formation at hematite surfaces by molecular functionalization probed by XUV reflection–absorption spectroscopy. *J. Chem. Phys.* **2019**, *151*, 104701.
- (9) Zhang, J.; Eslava, S. Understanding charge transfer, defects and surface states at hematite photoanodes. *Sustainable Energy & Fuels* **2019**, *3*, 1351–1364.
- (10) Yan, B.; Wan, D.; Chi, X.; Li, C.; Motapothula, M. R.; Hooda, S.; Yang, P.; Huang, Z.; Zeng, S.; Ramesh, A. G.; Pennycook, S. J.; Rusydi, A.; Ariando, Martin, J.; Venkatesan, T. Anatase TiO₂ a model system for large polaron transport. *ACS Appl. Mater. Interfaces* **2018**, *10*, 38201–38208.
- (11) Carneiro, L. M.; Cushing, S. K.; Liu, C.; Su, Y.; Yang, P.; Alivisatos, A.; Leone, S. R. Excitation-wavelength-dependent small polaron trapping of photoexcited carriers in α -Fe₂O₃. *Nat. Mater.* **2017**, *16*, 819–825.
- (12) Gregoire, J. M.; Zhou, L.; Haber, J. A. Combinatorial synthesis for AI-driven materials discovery. *Nat. Synth.* **2023**, *2*, 493–504.
- (13) Zhao, T.; Liu, Q.-L.; Zhao, Z.-Y. High-throughput screening delafossite CuMO₂ (M = IIIA, 3d, 4d, 5d, and RE) optoelectronic functional materials based on first-principles calculations. *J. Phys. Chem. C* **2019**, *123*, 14292–14302.
- (14) Wolf, M.; Madsen, G. K. H.; Dimopoulos, T. Accelerated screening of Cu-Ga-Fe oxide semiconductors by combinatorial spray deposition and high-throughput analysis. *Materials Advances* **2023**, *4*, 2612–2624.
- (15) Saadi, S.; Bouguelia, A.; Trari, M. Photocatalytic hydrogen evolution over CuCrO₂. *Sol. Energy* **2006**, *80*, 272–280.
- (16) Husek, J.; Cirri, A.; Biswas, S.; Asthagiri, A.; Baker, L. R. Hole thermalization dynamics facilitate ultrafast spatial charge separation in CuFeO₂ solar photocathodes. *J. Phys. Chem. C* **2018**, *122*, 11300–11304.
- (17) Husek, J.; Cirri, A.; Biswas, S.; Baker, L. R. Surface electron dynamics in hematite (α -Fe₂O₃): correlation between ultrafast surface electron trapping and small polaron formation. *Chem. Sci.* **2017**, *8*, 8170–8178.
- (18) Vura-Weis, J.; Jiang, C.-M.; Liu, C.; Gao, H.; Lucas, J. M.; de Groot, F. M. F.; Yang, P.; Alivisatos, A. P.; Leone, S. R. Femtosecond M_{2,3}-edge spectroscopy of transition-metal oxides: Photoinduced oxidation state change in α -Fe₂O₃. *J. Phys. Chem. Lett.* **2013**, *4*, 3667–3671.
- (19) Klobes, B.; Herlitschke, M.; Rushchanskii, K. Z.; Wille, H.-C.; Hummer, T. T. A.; van Loosdrecht, P. H. M.; Nugroho, A. A.; Hermann, R. P. Anisotropic lattice dynamics and intermediate-phase magnetism in delafossite CuFeO₂. *Phys. Rev. B* **2015**, *92*, 014304.
- (20) de Mello, E. V. L.; Ranninger, J. Dynamical properties of small polarons. *Phys. Rev. B* **1997**, *55*, 14872–14885.
- (21) Fitzmorris, B. C.; Patete, J. M.; Smith, J.; Mascorro, X.; Adams, S.; Wong, S. S.; Zhang, J. Z. Ultrafast transient absorption studies of hematite nanoparticles: The effect of particle shape on exciton dynamics. *ChemSusChem* **2013**, *6*, 1907–1914.
- (22) Joly, A. G.; Williams, J. R.; Chambers, S. A.; Xiong, G.; Hess, W. P.; Laman, D. M. Carrier dynamics in α -Fe₂O₃ (0001) thin films and single crystals probed by femtosecond transient absorption and reflectivity. *J. Appl. Phys.* **2006**, *99*, 053521.
- (23) Chen, Y.-J.; Okazaki, M.; Furube, A.; Chen, L.-Y. Ultrafast timescale charge carrier dynamics in nanocomposite hematite photoelectrodes. *J. Photochem. Photobiol., A* **2023**, *442*, 114820.
- (24) Zürich, M.; Chang, H.-T.; Borja, L. J.; Kraus, P. M.; Cushing, S. K.; Gandman, A.; Kaplan, C. J.; Oh, M. H.; Prell, J. S.; Prendergast, D.; Pemmaraju, C. D.; Neumark, D. M.; Leone, S. R. Direct and simultaneous observation of ultrafast electron and hole dynamics in germanium. *Nat. Commun.* **2017**, *8*, 15734.
- (25) Cushing, S. K.; Lee, A.; Molesky, I. J. P.; Carneiro, L. M.; Chang, H.-T.; Zürich, M.; Leone, S. R. Differentiating photoexcited carrier and phonon dynamics in the Δ , L, and Γ valleys of Si(100) with transient extreme ultraviolet spectroscopy. *J. Phys. Chem. C* **2019**, *123*, 3343–3352.
- (26) de Roulet, B. R.; Drescher, L.; Sato, S. A.; Leone, S. R. Initial electron thermalization in metals measured by attosecond transient absorption spectroscopy. *Phys. Rev. B* **2024**, *110*, 174301.
- (27) Liu, H.; Michelsen, J. M.; Mendes, J. L.; Klein, I. M.; Bauers, S. R.; Evans, J. M.; Zakutayev, A.; Cushing, S. K. Measuring photoexcited electron and hole dynamics in ZnTe and modeling excited state core-valence effects in transient extreme ultraviolet reflection spectroscopy. *J. Phys. Chem. Lett.* **2023**, *14*, 2106–2111.
- (28) Kim, Y.-J.; Mendes, J. L.; Michelsen, J. M.; Shin, H. J.; Lee, N.; Choi, Y. J.; Cushing, S. K. Coherent charge hopping suppresses photoexcited small polarons in ErFeO₃ by antiadiabatic formation mechanism. *Sci. Adv.* **2024**, *10*, adk4282.
- (29) Mendes, J. L.; Shin, H. J.; Seo, J. Y.; Lee, N.; Choi, Y. J.; Varley, J. B.; Cushing, S. K. Dynamic competition between hubbard and superexchange interactions selectively localizes electrons and holes through polarons. *J. Am. Chem. Soc.* **2025**, *147*, 16018–16026.
- (30) Klein, I. M.; Liu, H.; Nimlos, D.; Krotz, A.; Cushing, S. K. Ab initio prediction of excited-state and polaron effects in transient XUV measurements of α -Fe₂O₃. *J. Am. Chem. Soc.* **2022**, *144*, 12834–12841.
- (31) Stavitski, E.; de Groot, F. M. The CTM4XAS program for EELS and XAS spectral shape analysis of transition metal L edges. *Micron* **2010**, *41*, 687–694.
- (32) Holstein, T. Studies of polaron motion. *Ann. Phys.* **1959**, *8*, 325–342.
- (33) Chen, H.-W.; Huang, C.-Y.; Shu, G.-J.; Liu, H.-L. Temperature-dependent optical properties of CuFeO₂ through the structural phase transition. *RSC Adv.* **2021**, *11*, 40173–40181.
- (34) Ahart, C. S.; Rosso, K. M.; Blumberger, J. Electron and hole mobilities in bulk hematite from spin-constrained density functional theory. *J. Am. Chem. Soc.* **2022**, *144*, 4623–4632.
- (35) Ferri, M.; Elliott, J.; Farnesi Camellone, M.; Fabris, S.; Piccinin, S. Thermodynamic stability and native point defects of CuFeO₂ photocathodes in dry and electrochemical environments. *J. Phys. Chem. C* **2019**, *123*, 29589–29598.
- (36) Ahart, C. S.; Blumberger, J.; Rosso, K. M. Polaronic structure of excess electrons and holes for a series of bulk iron oxides. *Phys. Chem. Chem. Phys.* **2020**, *22*, 10699–10709.
- (37) Naveas, N.; Pulido, R.; Marini, C.; Hernández-Montelongo, J.; Silván, M. M. First-principles calculations of hematite (α -Fe₂O₃) by self-consistent DFT+U+V. *iScience* **2023**, *26*, 106033.
- (38) Li, T.; Yan, Y.; Shi, Q. A low-temperature quantum Fokker-Planck equation that improves the numerical stability of the hierarchical equations of motion for the Brownian oscillator spectral density. *J. Chem. Phys.* **2022**, *156*, 064107.
- (39) Zuehlsdorff, T. J.; Montoya-Castillo, A.; Napoli, J. A.; Markland, T. E.; Isborn, C. M. Optical spectra in the condensed phase: Capturing anharmonic and vibronic features using dynamic and static approaches. *J. Chem. Phys.* **2019**, *151*, 074111.
- (40) Wiethorn, Z. R.; Hunter, K. E.; Zuehlsdorff, T. J.; Montoya-Castillo, A. Beyond the Condon limit: Condensed phase optical spectra from atomistic simulations. *J. Chem. Phys.* **2023**, *159*, 244114.

- (41) Li, H.; Guo, M.; Zhou, Z.; Long, R.; Fang, W.-H. Excitation-wavelength-dependent charge-carrier lifetime in hematite: An insight from nonadiabatic molecular dynamics. *J. Phys. Chem. Lett.* **2023**, *14*, 2448–2454.
- (42) Wiethorn, Z. R.; Hunter, K. E.; Montoya-Castillo, A.; Zuehlisdorff, T. J. Symmetry breaking fluctuations split the porphyrin Q bands. *arXiv:2411.02687* **2024**, DOI: 10.48550/arXiv.2411.02687.
- (43) Dekker, H. Noninteracting-blip approximation for a two-level system coupled to a heat bath. *Phys. Rev. A* **1987**, *35*, 1436–1437.
- (44) Bhattacharyya, S.; Sayer, T.; Montoya-Castillo, A. Space-local memory in generalized master equations: Reaching the thermodynamic limit for the cost of a small lattice simulation. *J. Chem. Phys.* **2025**, *162*, 091102.
- (45) Bhattacharyya, S.; Sayer, T.; Montoya-Castillo, A. Anomalous transport of small polarons arises from transient lattice relaxation or immovable boundaries. *J. Phys. Chem. Lett.* **2024**, *15*, 1382–1389.
- (46) Hannewald, K.; Stojanović, V. M.; Schellekens, J. M. T.; Bobbert, P. A.; Kresse, G.; Hafner, J. Theory of polaron bandwidth narrowing in organic molecular crystals. *Phys. Rev. B* **2004**, *69*, 075211.
- (47) Ortmann, F.; Bechstedt, F.; Hannewald, K. Theory of charge transport in organic crystals: Beyond Holstein's small-polaron model. *Phys. Rev. B* **2009**, *79*, 235206.
- (48) Bhattacharyya, S.; Sayer, T.; Montoya-Castillo, A. Non-equilibrium relaxation exponentially delays the onset of quantum diffusion. *Proc. Natl. Acad. Sci. U. S. A.* **2025**, *122*, e2424582122.
- (49) Delor, M.; Weaver, H. L.; Yu, Q.; Ginsberg, N. S. Imaging material functionality through three-dimensional nanoscale tracking of energy flow. *Nat. Mater.* **2020**, *19*, 56–62.
- (50) Weaver, H. L.; Went, C. M.; Wong, J.; Jasrasaria, D.; Rabani, E.; Atwater, H. A.; Ginsberg, N. S. Detecting, distinguishing, and spatiotemporally tracking photogenerated charge and heat at the nanoscale. *ACS Nano* **2023**, *17*, 19011–19021.
- (51) Lejman, M.; Vaudel, G.; Infante, I. C.; Gemeiner, P.; Gusev, V. E.; Dkhil, B.; Ruello, P. Giant ultrafast photo-induced shear strain in ferroelectric BiFeO₃. *Nat. Commun.* **2014**, *5*, 4301.
- (52) Raiser, D.; Mildner, S.; Ifland, B.; Sotoudeh, M.; Blöchl, P.; Techert, S.; Jooss, C. Evolution of hot polaron states with a nanosecond lifetime in a manganite perovskite. *Adv. Energy Mater.* **2017**, *7*, 1602174.