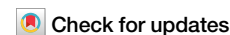


<https://doi.org/10.1038/s43246-025-00909-w>

Dynamic control of X-ray core-exciton resonances by Coulomb screening in photoexcited semiconductors



Thomas C. Rossi^{1,13}✉, Lu Qiao^{2,13}✉, Conner P. Dykstra³, Ronaldo Rodrigues Pela⁴, Richard Gnewkow^{5,6}, Rachel F. Wallick³, John H. Burke³, Erin Nicholas³, Anne Marie March⁷, Gilles Doumy⁷, D. Bruce Buchholz⁸, Christiane Deparis⁹, Jesús Zúñiga-Pérez^{9,10}, Michael Weise¹¹, Klaus Ellmer¹¹, Mattis Fondell¹², Claudia Draxl² & Renske M. van der Veen^{1,3,6}

Excitonics is an emerging field focused on exploiting and manipulating excitons generated through light-matter interactions. Advancing the field into X-ray excitonics requires precise energy and time control of core-exciton resonances, enabling non-linear X-ray phenomena such as element-specific X-ray transient gratings, and advancing material characterization. To achieve these objectives, it is essential to comprehend the role of many-body effects governing core-exciton dynamics. In this work, we address this challenge by combining experiments with an *ab initio* approach specifically developed to interpret pump-probe excitations. Applied to the prototypical wide-bandgap semiconductor ZnO, first-principles calculations reproduce experimental results and unveil how the density and distribution of photoexcited carriers dynamically tune Coulomb screening, thereby controlling core-exciton binding energies, while Pauli blocking remains negligible. These insights inform a method for dynamically controlling core-exciton resonances at absorption edges, achieving either a uniform spectral blue shift caused by thermalized carrier distributions on picosecond timescales, or distinct blue shifts for individual resonances, driven by time-dependent carrier distributions on femtosecond timescales.

Excitons are electron-hole pairs bound by attractive Coulomb forces. These neutral quasiparticles typically form across the bandgap of photoexcited semiconductors¹. Excitonics is an emerging field that explores the manipulation of excitons, primarily in the optical spectral range², with a recent extension to the extreme ultraviolet³. Advancing the principles of excitonics into the X-ray regime requires controlling core excitons formed between localized core holes and delocalized valence electrons. Core excitons dominate light absorption in X-ray absorption spectra (XAS) near the absorption edge of semiconductors⁴. Many-body effects shape these resonances^{5–7}, complicating the interpretation of core-level spectra in experiments. The strength of Coulomb screening determines exciton binding energies and the distribution of electron-hole wavefunctions^{8–10}, thereby influencing the energies and widths of core-exciton resonances⁵. However, the role of time-dependent Coulomb screening on core excitons, driven by dynamic carrier populations, remains largely unexplored.

In this study, taking zinc oxide (ZnO) as a prototypical wide-bandgap semiconductor material, we combine experiment and theory to investigate the effect of time-dependent Coulomb screening on core-exciton dynamics

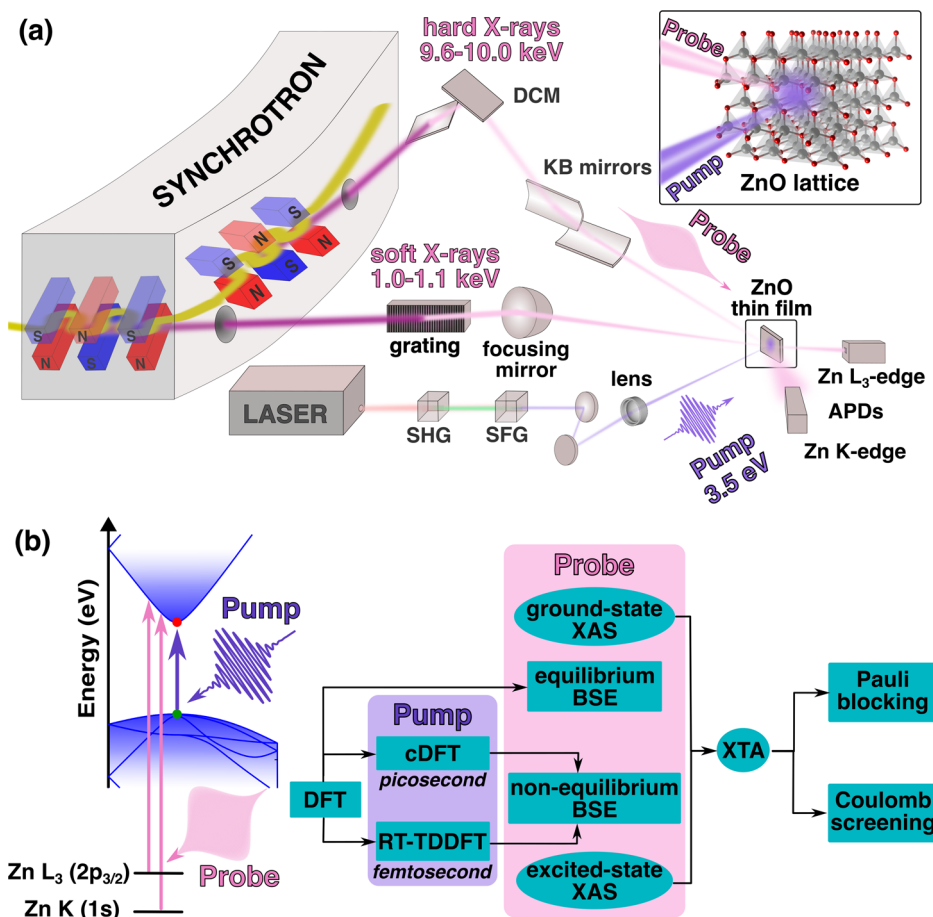
following photoexcitation. To this end, we perform pump-probe picosecond X-ray transient absorption (XTA) spectroscopy at synchrotrons, probing two different absorption edges, to capture the time-resolved response of core excitons to photoexcited carriers generated by a laser pulse (Fig. 1a). Although advanced experimental XTA setups can effectively capture the time evolution of core excitons¹¹, investigating their dynamics remains a significant challenge for *ab initio* methods.

Theoretical modeling of core-exciton dynamics requires an *ab initio* approach capable of capturing time-dependent many-body effects. Existing methodologies primarily focus on the response of optical excitons to pump excitations^{7,12,13}. Real-time time-dependent density-functional theory (RT-TDDFT), while widely used in pump-probe simulations^{12,13}, lacks an explicit treatment of many-body interactions, which limits its accuracy in describing exciton dynamics. Excitonic Bloch equations can capture the initial transient response driven by external laser fields, but neglect time-dependent energy renormalization and screening effects¹⁴. Non-equilibrium Green functions provide a rigorous treatment of time-dependent many-body effects; however, due to the high computational costs involved, extensive

A full list of affiliations appears at the end of the paper. ✉e-mail: thomas.rossi@helmholtz-berlin.de; qiaolu@physik.hu-berlin.de

Fig. 1 | Experimental setup and theoretical workflow for the dynamic control of core excitons.

a Experimental setup used to measure pump-probe XTA spectra of ZnO (0001) thin films. DCM double crystal monochromator, SHG second harmonic generation, SFG sum frequency generation, KB: Kirkpatrick-Baez focusing mirrors, APDs avalanche photodiodes. **b** Theoretical workflow to simulate XTA spectra and disentangle many-body effects (Pauli blocking and Coulomb screening).



approximations and simplifications are unavoidable^{15,16}. While these approaches are used to describe the response of optical excitons to photo-induced perturbations, core-exciton dynamics remain unaddressed. To tackle this challenge, we develop a novel *ab initio* approach, integrating constrained density-functional theory (cDFT), RT-TDDFT, and a non-equilibrium formalism based on the Bethe-Salpeter equation (BSE), as depicted in the workflow in Fig. 1b.

The combined experimental and theoretical investigation presented here offers profound insights into the time-dependent response of core excitons to pump excitation, providing strategies for their dynamic control through Coulomb screening. Core excitons can be exploited to generate resonant transient gratings, enabling bulk- and element-specific sensitivity¹⁷. This capability makes them a promising tool for probing local electronic and lattice dynamics through X-ray four-wave mixing, particularly in the study of local coherences and population effects¹⁸. In addition, core excitons play a central role in precision spectroscopy for materials characterization¹⁹, as their spectral features are highly sensitive to Coulomb screening effects, which are strongly influenced by the density of free carriers.

Results and discussion

Ab initio approach to XTA spectra

The theoretical method developed here goes beyond the standard BSE, by incorporating time-dependent carrier densities and distributions in photoexcited states obtained through cDFT and RT-TDDFT (Fig. 1b). The formalisms are detailed in the Supplementary section 1. (i) For picosecond time delays following optical pumping, the carrier occupations are determined using cDFT, where carriers follow a Fermi-Dirac distribution at the lattice temperature, populating the conduction-band minimum (CBM) and valence-band maximum. Thermalized carrier distributions serve as valid approximations for photoexcited materials at time delays considerably longer than the characteristic timescales of electron-electron²⁰,

electron-phonon²¹, and phonon-phonon scattering²². (ii) For femtosecond time delays, the carrier occupations are determined using RT-TDDFT, incorporating experimental parameters of the pump pulse, such as frequency, fluence, duration, and polarization. This method enables the simulation of time-dependent carrier populations driven by laser fields, where excited electrons and holes populate multiple states in phase space. Excited-state occupations obtained from cDFT and RT-TDDFT are subsequently employed in BSE calculations to model the interaction of the X-ray probe with the photoexcited material. Finally, XTA spectra are computed as the difference between the XAS spectra under non-equilibrium and equilibrium conditions.

Experimental approach to XTA spectra

Experimental XTA spectra are measured with a pump-probe setup illustrated in Fig. 1a. Pump pulses from the third harmonic of a near-infrared laser (~3.5 eV) excite ZnO (0001) thin films above their bandgap (~3.3 eV), generating electron-hole pairs (thin-film characterizations in Supplementary section 2). Monochromatized X-ray probe pulses either at the Zn K- or L₃-edge are synchronized with the laser pump pulses to measure XAS spectra in the photoexcited state of ZnO (experimental setup described in Methods and in Supplementary section 3). The time delay between the pump and the probe is set to 100 ± 10 ps corresponding to the time resolution of the instrument, limited by the duration of the X-ray probe pulses (~70 ps). Time traces are reported in Supplementary section 4 showing that samples relax back to equilibrium after the initial excitation between consecutive pump pulses.

Comparison between experimental and calculated spectra

Before discussing XTA spectra, we first examine the equilibrium XAS spectra at the Zn K- and L₃-edge, observing that XAS spectra calculated using BSE reproduce well the experimental counterparts, as displayed in

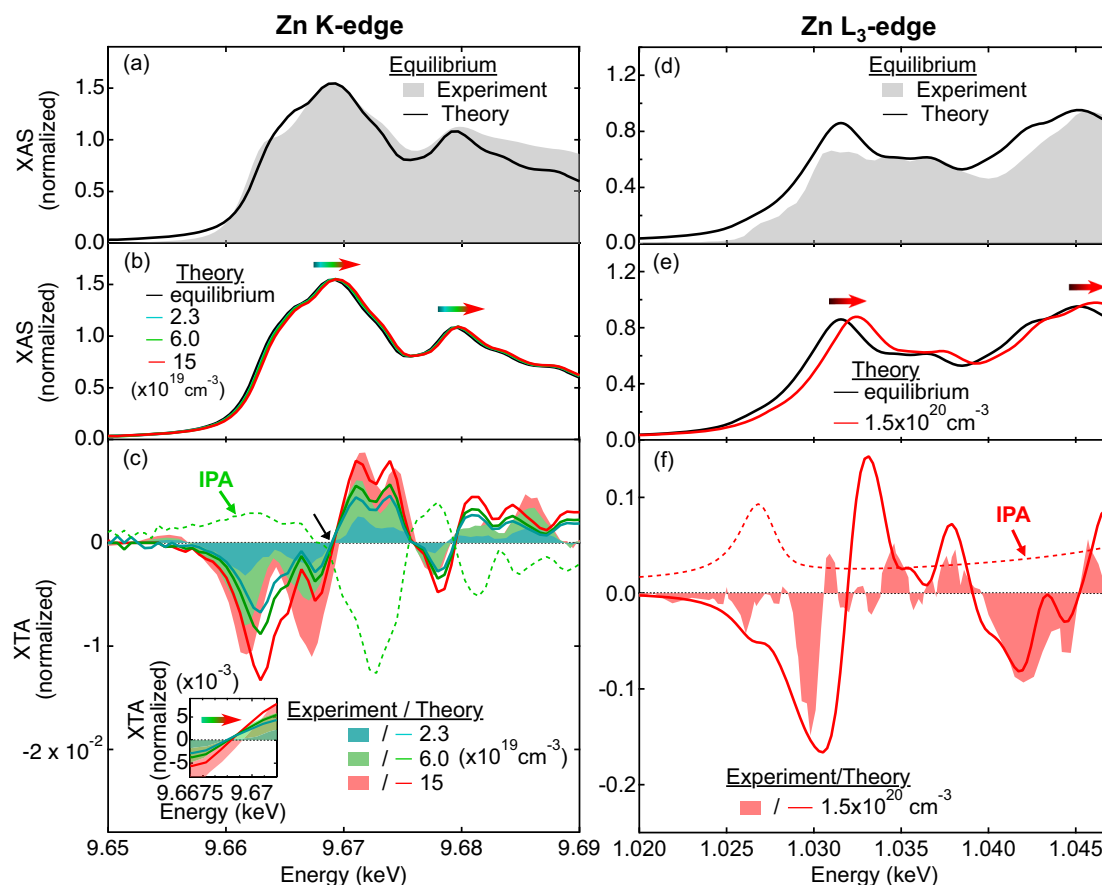


Fig. 2 | Photoexcited carriers lead to a blue shift of excited-state XAS spectra at picosecond timescales. **a, d** Normalized equilibrium XAS spectra at the Zn K- and L₃-edge of ZnO from experiments (gray shaded curves) and BSE calculations (black curves). **b, e** Calculated normalized excited-state XAS spectra using cDFT+BSE with excitation densities ranging from $2.3 \times 10^{19} \text{ cm}^{-3}$ to $1.5 \times 10^{20} \text{ cm}^{-3}$ (colored curves). The computed equilibrium spectrum is shown for reference (black curves). **c, f** Comparison of calculated

(colored curves) and experimental (shaded colored areas) normalized XTA spectra at 100 ps for comparable excitation densities (same color coding). Vertical scaling factors of 0.125 and 2.2 are applied to the calculated XTA spectra at the Zn K- and L₃-edge, respectively. Calculated XTA spectra within the IPA are shown for reference (dashed curves, same color coding). Inset: magnification of the calculated Zn K-edge XTA spectra at $\sim 9.670 \text{ keV}$ (region marked by a black arrow).

Fig. 2a, d (background subtraction and normalization procedures detailed in Supplementary section 5). Non-equilibrium XAS spectra, calculated using the cDFT+BSE approach, demonstrate that thermalized excited carriers distributions result in an increasing blue shift of the spectral features as the excitation density increases (Fig. 2b, e). The XTA spectra, derived from the difference between non-equilibrium and equilibrium XAS, are presented in Fig. 2c, f. Experimental XTA curves, from which contributions from lattice heating have been removed (for details, see ref. 23 and the Supplementary section 6), are depicted in Fig. 2c, f as well. The good agreement between the calculated and experimental XTA spectra (full lines and shaded areas, respectively) is evident. In contrast, XTA spectra calculated within the independent particle approximation (IPA, colored dashed lines) do not align with the measured counterparts, qualitatively or quantitatively. This discrepancy underscores that the spectral blue shift caused by the interaction between photoexcited carriers and the core hole can only be explained when many-body interactions are incorporated into the calculations.

Disentangling many-body effects

Many-body effects play a crucial role in the XAS spectra of photoexcited semiconductors. To gain insight into core-exciton dynamics, it is essential to incorporate many-body effects, such as Pauli blocking and Coulomb screening, and understand how each contribution tailors XTA spectra. Pauli blocking arises from the exclusion principle, which prohibits excitations to occupied states. Coulomb screening refers to the reduction of the effective Coulomb interactions between core holes and excited electrons caused by the screening of free carriers. To isolate the effect of Pauli blocking

(Coulomb screening), we incorporate excited-state occupations only to evaluate the dipole moment matrix (screened Coulomb interaction), details in equation 18–19 in Supplementary section 1.

Figure 3 shows that, for thermalized carrier distributions, Coulomb screening (shaded blue area) prevails over Pauli blocking (shaded red area) at both the Zn K- and L₃-edges. In this case, Pauli blocking is dominated by the change in the exchange interaction. A similar trend is observed for non-thermal carrier distributions at ultrashort time delays (Supplementary Fig. S18), where phase-space filling becomes the primary mechanism behind Pauli blocking. These results highlight the dominant role of Coulomb screening by photoexcited carriers in core-exciton dynamics, which should a priori affect any core-level transition and can be used as a sensitive probe of photoexcited carriers. These conclusions are also consistent with recent RT-TDDFT studies suggesting that electronic screening of the core hole plays a role in shaping XTA spectra at the M-edge of photoexcited transition metals^{24,25} and low-bandgap semiconductors²⁶.

Finally, we observe that Coulomb screening reduces the exciton binding energy (Fig. 4a), while the single-particle gap remains nearly unchanged following pump excitation (Supplementary Fig. S23). As a result, the exciton resonance energy increases, leading to the observed blue shift in the excited-state XAS spectra (Fig. 2b, e).

Picosecond control of core-exciton screening

In Fig. 2c, non-linearities in the variation of the experimental XTA amplitude are apparent, for instance, in the relative amplitude change of the two negative features at ~ 9.662 and $\sim 9.667 \text{ keV}$ with the excitation fluence. Yet,

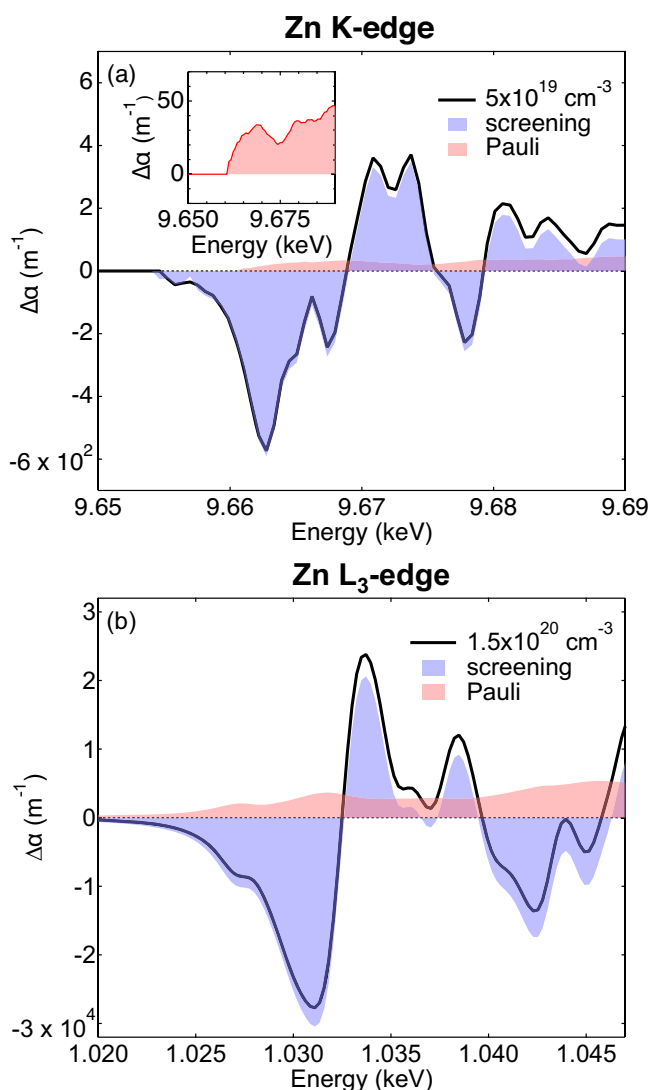


Fig. 3 | XTA spectra dominated by the effect of core-exciton Coulomb screening of photoexcited carriers. Calculated contributions of the Coulomb screening (shaded blue areas) and Pauli blocking (shaded red areas) by photoexcited carriers to the XTA spectra (black curves) at the **a** Zn K-edge and **b** Zn L₃-edge at a time delay of 100 ps. Inset: Pauli blocking contribution at the Zn K-edge.

cDFT+BSE can reproduce these changes to a certain extent, as indicated by the non-unique zero-crossing point ~ 9.67 keV in the experiment and calculations (inset of Fig. 2c).

To inspect closer this nonlinear behavior, we present in Fig. 4b the evolution of the measured XTA amplitude with the excitation fluence. There is a weak saturation, particularly visible at carrier densities above $\sim 1 \times 10^{20} \text{ cm}^{-3}$ and from the linear interpolation of the amplitude to zero excitation density (colored arrows). This nonlinearity is well captured by the cDFT+BSE calculations (Fig. 4c). The calculations reveal a pronounced nonlinearity at low excitation densities, primarily due to the non-negligible contribution of Pauli blocking relative to Coulomb screening (see Supplementary Fig. S17). As the excitation density increases, Coulomb screening becomes progressively more important, consistent with previous observations²³. These results indicate that at low excitation densities ($\sim 1 \times 10^{17} - 1 \times 10^{19} \text{ cm}^{-3}$), the nonlinear response arises mainly from a shifting balance between Pauli blocking and Coulomb screening. In contrast, at high excitation densities ($> 1 \times 10^{19} \text{ cm}^{-3}$), it originates from the nonlinear behavior of Coulomb screening. Figure 4a connects the nonlinear effect of Coulomb screening to a saturated reduction of the calculated

binding energy of the core exciton formed between the Zn 1s core level and the CBM+1 state around the Γ -point.

To investigate the nonlinear dependence of the core-exciton screening on the excitation density more deeply, we examine the effect of excited carrier distributions in phase space. Three idealized modeled distributions are depicted in Fig. 4d–f with the same excitation density of $5.0 \times 10^{19} \text{ cm}^{-3}$. In panel (d) only the Γ -point is populated, while in panels (e) and (f) only 41.2% and 30%, respectively, of the excited electrons are at the Γ -point, and the remaining electrons extend farther out in k -space following a Fermi-Dirac distribution. The corresponding calculated XTA spectra in Fig. 4g reveal that an increased delocalization of carrier distributions in phase space reduces the amplitude of the XTA spectra, which is a consequence of a lower core-exciton screening. However, these three modeled distributions do not account for the dynamic nature of carrier distributions under experimental conditions. Rather, they are intended to provide physical insight into the effect of carrier delocalization on core-exciton screening.

We conclude that core-exciton resonances in XAS spectra can be dynamically controlled by both carrier densities and their distributions in phase space. These two parameters can be further used to control core-exciton screening with tunable excitation pulses on much shorter timescales, as will be discussed in the next section. Reciprocally, combining experiment and theory could be used to yield local carrier concentrations and distributions of photoexcited semiconductors, similar to the method proposed in a recent work²⁷, or under operando conditions.

Femtosecond control of core-exciton screening

Picosecond XTA spectra have demonstrated how core-exciton screening is determined by thermalized carrier distributions, which intrinsically limits the degree of control over core-exciton resonances. These results drive the investigation of core-exciton screening at femtosecond timescales with dynamic carrier densities and distributions. In this context, the RT-TDDFT+BSE approach developed in this work can model time-dependent carrier populations, providing guidelines for the dynamic control of core excitons at ultrashort timescales, a capability beyond the reach of the cDFT+BSE approach.

Initially, we adopt pump pulses with 3.49 eV photon energy, fluences from 7.7 to 85.3 mJ cm^{-2} , and pulse duration of 10 fs in the RT-TDDFT calculations. During the interaction between the pump pulse and the sample (0–20 fs), time-dependent carrier densities and distributions lead to complex variations of the XAS spectrum (Fig. 5a). At 20 fs and beyond, carrier-carrier scattering is completed, which leads to a convergence of the spectral lineshape (Fig. 5a, dark blue line, and green dots) and a globally blue-shifted version of the equilibrium XAS spectrum.

On the femtosecond timescale, the evolving excited carriers contribute to a “shuffling” of exciton resonances: individual peaks undergo different degrees of screening, leading to different energy shifts (see discussion in Supplementary section 7.2 and Fig. S22). These individual shifts distort the lineshape of excited-state XAS spectra, making them differ significantly from the equilibrium spectrum (Fig. 5a), far beyond what is observed on picosecond timescales (Fig. 2b). The pronounced change in spectral shape is attributed to the delocalized carrier distribution in the Brillouin zone on femtosecond timescales, as shown in the Supplementary Fig. S20. For instance, calculated XTA spectra at 20 fs (Fig. 5b) exhibit amplitudes typically an order of magnitude larger than at 100 ps under comparable excitation fluences (Fig. 2c), indicating a much larger core-exciton screening and blue shift of exciton resonances. This difference can be attributed to significantly higher photoexcited carrier populations at time delays shorter than the electron-hole recombination time²⁸: here, for the fluence of $\sim 75 \text{ mJ cm}^{-2}$, the carrier density decreases from $5 \times 10^{21} \text{ cm}^{-3}$ at 20 fs (Supplementary Fig. S19a) to $1.5 \times 10^{20} \text{ cm}^{-3}$ at 100 ps. These drastic changes suggest novel opportunities for exploring dynamical core-exciton screening on ultrashort delays, where carrier densities are expected to exceed significantly those on picosecond timescales, resulting in more pronounced core-exciton screenings.

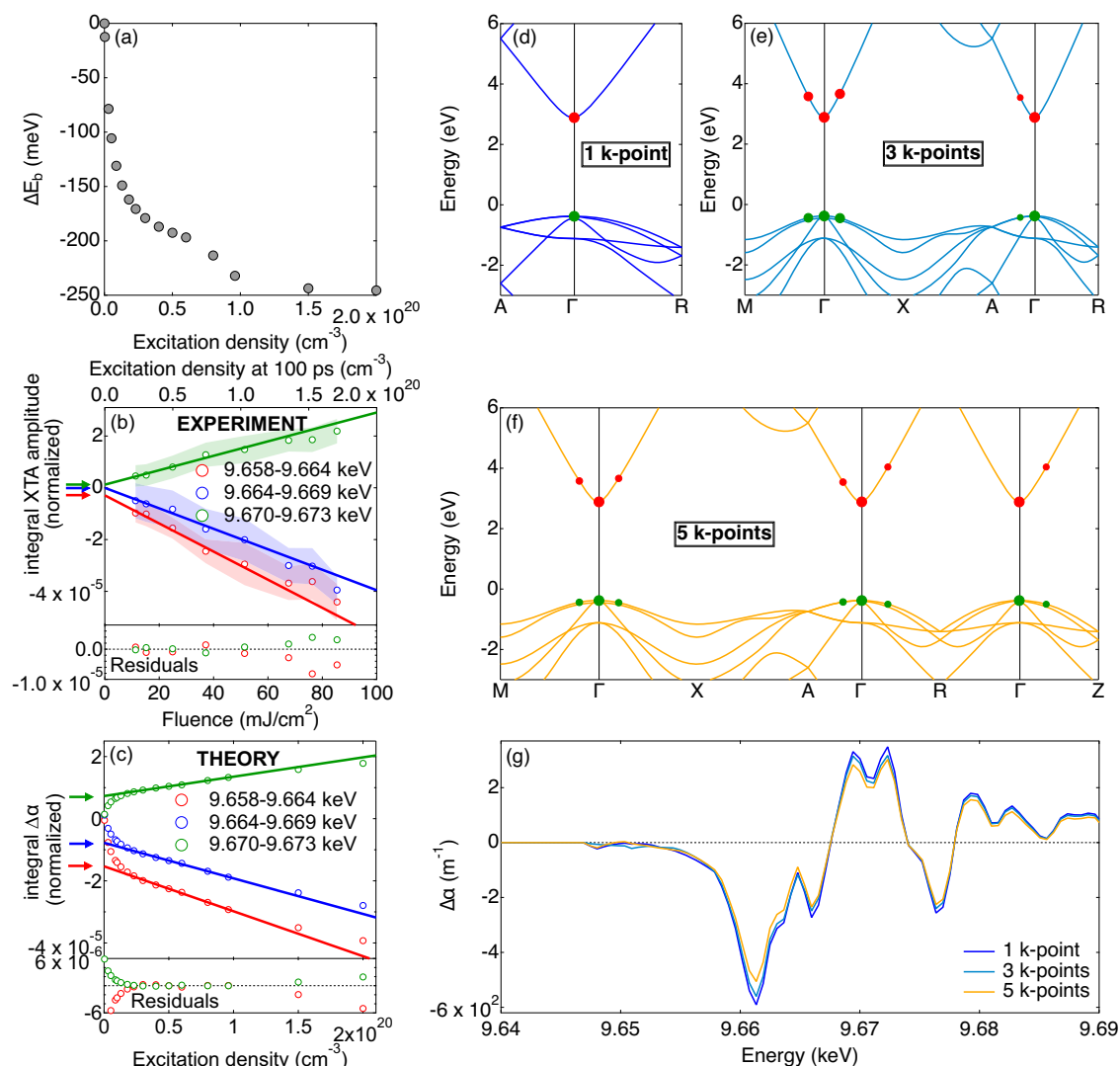


Fig. 4 | Control over core-exciton screening with carrier density and distribution. **a** Computed change in core-exciton binding energy (ΔE_b) as a function of excitation density with respect to the equilibrium exciton binding energy (734 meV). **b** Evolution of the integrated XTA amplitude as a function of excitation fluence over the energy ranges 9.658–9.664 keV (red circles), 9.664–9.669 keV (blue circles), and 9.670–9.673 keV (green circles). The shaded areas represent confidence intervals based on the integration of the XTA amplitude within one standard deviation. Linear fittings are weighted by the confidence intervals and constrained to fluences $<50 \text{ mJ cm}^{-2}$. Details of the experimental excitation density calculation in Supplementary section 8, fluence dependence data in Supplementary section 9. **c** Computed integral of the normalized XTA amplitude using the cDFT+BSE

method as a function of excitation density over the same energy range and color coding. Lines are linear fits constrained to excitation densities between $2 \times 10^{19} \text{ cm}^{-3}$ and $1 \times 10^{20} \text{ cm}^{-3}$, showing the sub-linearity of the calculated XTA amplitude. **b, c** colored arrows show the interpolated amplitude at zero excitation density from the linear fits. Residuals of the linear fits are in the lower panels. **d–f** Distributions of photoexcited electrons (red circles) and holes (green circles) over **(d)** 1, **(e)** 3, and **(f)** 5 k-points at a fixed excitation density of $5.0 \times 10^{19} \text{ cm}^{-3}$. The area of the circles is proportional to the occupation at a given k-point. **g** Computed XTA spectra with cDFT+BSE for the different carrier distributions in **(d–f)** with the same color coding.

The RT-TDDFT approach enables us to analyze how the pump fluence can be used to tailor core-exciton resonances on ultrafast timescales. In a different context, it has been observed that the pump fluence is a crucial parameter in controlling the conductivity of (photo)piezoelectronic materials such as ZnO ²⁹. Figure 5b displays XTA spectra calculated at 20 fs for various fluences (solid lines), comparing them with the XTA at 100 ps (shaded gray) for a fluence of 76.4 mJ cm^{-2} (carrier density of $1.5 \times 10^{20} \text{ cm}^{-3}$). A large variation in the XTA spectral lineshape is observed with increasing fluence, as the amplitude of the negative feature at 9.677 keV increases more significantly compared to the negative feature at 9.671 keV (red and black dashed lines in Fig. 5b). This evolution demonstrates that the dynamic control of core-exciton screening is achieved on femtosecond timescales, driven by time-dependent carrier distributions, which have no equivalent with thermalized carrier distributions on picosecond timescales.

This capability of dynamical control by Coulomb screening paves the way for the development of transient excitonic states, which remain out-of-reach with thermodynamic parameters.

Besides pump fluences, another factor that impacts core-exciton resonances is the polarization of the probe beam: it enables the selective study of excitons with specific orientations of the transition dipole moment with respect to the crystal lattice. For instance, it has been shown that screening of the core-hole potential is anisotropic in layered cobaltites³⁰ and cuprates³¹. Our RT-TDDFT+BSE simulations reveal that the spectral blue shift is always larger in the **(a,b)**-plane than along the **c**-axis (Fig. 5c–e) at any pump fluences, while the relative amplitude exhibits more significant variations along **c** (Fig. 5d), which is clearly visible in the XTA spectra (Supplementary Fig. S21). This observation indicates that excitons with transition dipole moments along **(a,b)** experience stronger transient

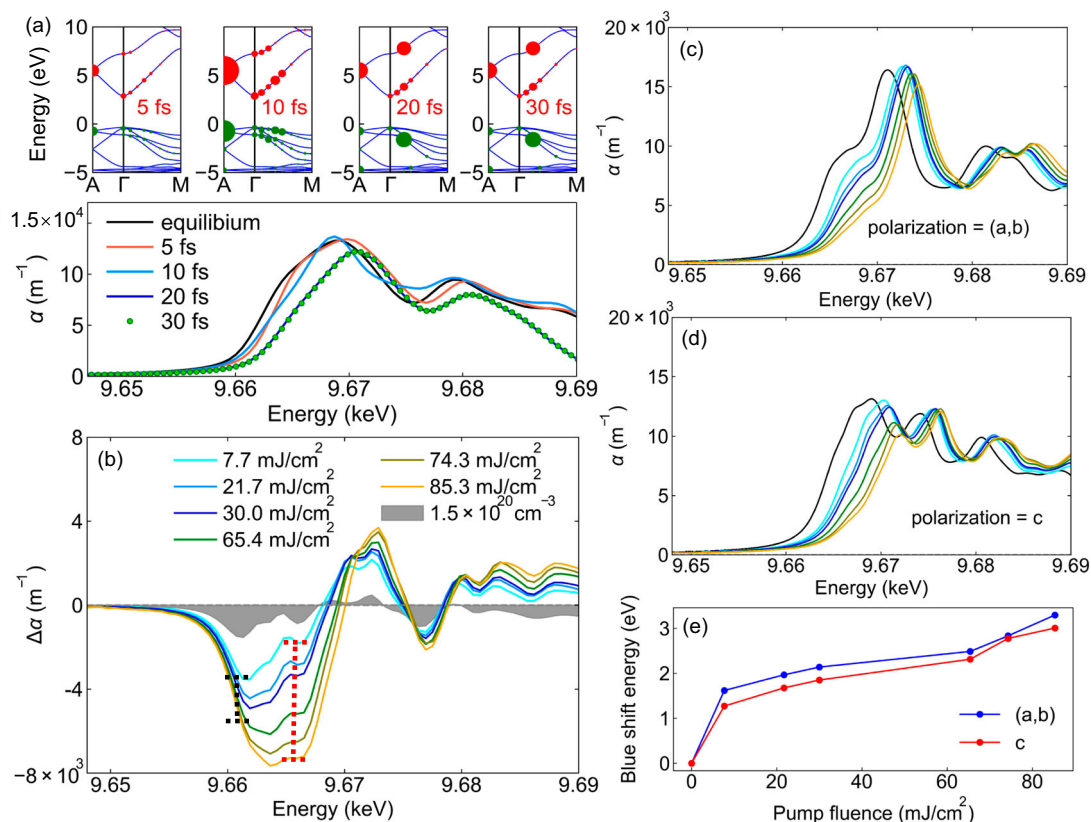


Fig. 5 | Femtosecond control of core-exciton resonances by Coulomb screening.

a Top panels: time evolution of excited electrons (red circles) and holes (green circles) distributions at 5, 10, 20, and 30 fs following optical pumping with fluence of 21.7 mJ cm⁻². Bottom panel: Corresponding calculated XAS spectra at the Zn K-edge show spectral evolution due to dynamical Coulomb screening. **b** Computed XTA spectra at 20 fs for various pump fluences from 7.7 to 85.3 mJ cm⁻² (colored

curves). The calculated XTA spectrum at 100 ps with an excitation density of $1.5 \times 10^{20} \text{ cm}^{-3}$ is shown for reference (shaded gray). **c, d** Computed excited-state XAS spectra with the probe polarization in (c) (a, b)-plane and **d** along the c-axis of the ZnO lattice for different pump fluences (same color coding as in b). **e** Blue shift of the first peak energy in the XAS spectra as a function of pump fluence for different probe polarizations: (a, b)-plane (blue) and c-axis (red).

Coulomb screening effects, which is opposite to the trend observed in the transient screening of optical excitons in ZnO³². Consequently, by adjusting the probe angle, we can observe variations of the core-exciton Coulomb screening due to anisotropic dielectric responses, which expands the portfolio of available parameters to control core-exciton resonances and their spectral characteristics through external perturbations. Such tunability holds great potential for tailoring X-ray photon responses and designing optimized excitonic features for applications in photonic and quantum technologies. The results are of fundamental importance for future experiments on semiconductor materials at X-ray free-electron lasers³³.

In summary, by combining a newly developed ab initio approach and experiment, we have demonstrated for the example of ZnO, how core-exciton resonances can be controlled by time-dependent Coulomb screening, depending on both the density and distribution of the photoexcited carriers (summarized in Fig. 6). Screening of the core hole reduces exciton binding energies, resulting in a blue shift of XAS spectra in the excited state. Our findings are broadly applicable to semiconductors, where photoexcitation does not result in localized carriers with weak contributions to Coulomb screening (such as polarons or trapped charges)^{34,35}. Time-dependent core-exciton screening provides a temporal probe of carrier densities with element specificity, making it a powerful tool for investigating charge transfer at interfaces³⁶ and in operando conditions³⁷. This work establishes a pathway for extending excitonics into the X-ray region, where core excitons with kiloelectronvolt resonances and binding energies of hundreds of millielectronvolts can be dynamically controlled by photoexcitation. Future experiments leveraging femtosecond X-ray free-electron lasers and tailored light fields could enable ultrafast dynamic control of core excitons, opening new opportunities in material characterization, nonlinear

X-ray optics and spectroscopy. The experimental and theoretical approaches proposed in this paper could also be applied to optical excitons, providing insights into their many-body interactions and enabling dynamic control over optical transitions.

Methods

X-ray absorption and X-ray transient absorption spectroscopy

XAS and XTA spectra at the Zn K-edge of ZnO thin films were acquired at the Advanced Photon Source (Argonne National Laboratory). The experimental setup has been extensively described in the Supplementary Information of ref. 23. The X-ray beam was *p*-polarized with ~ 70 ps pulses at an incidence angle of $45 \pm 2^\circ$ on the sample surface. The pump excitation was performed with the third harmonic (355 nm, 3.49 eV, *p*-polarization) of a Nd:YVO₄ Duetto laser (Time-Bandwidth products), which delivered ~ 10 ps pulses (FWHM) at 100.266 kHz. During the XAS and XTA measurements, a nitrogen flow was applied to the sample to prevent adsorption and diffusion of carbon impurities and water inside the material. The nitrogen flow also provided active cooling, preventing static heating caused by the laser excitation. Temperature-dependent XAS spectra were recorded with the sample on a heating stage (Linkam THMSG-600) between room temperature ($24 \pm 2^\circ \text{C}$) and $190 \pm 2^\circ \text{C}$.

XAS and XTA spectra at the Zn L₃-edge of ZnO thin films were acquired in transmission at the UE52-SGM beamline of BESSY II³⁸. The setup is described in ref. 39. The nmTransmission NEXAFS chamber was modified with a sample tip to allow for measurements of thin film samples in transmission. The X-ray beam was *p*-polarized, impinging at normal incidence on the sample surface. The pump laser consisted of 350 fs pulses at the third harmonic (343 nm, 3.61 eV, *p*-polarization) of a Yb-doped hybrid

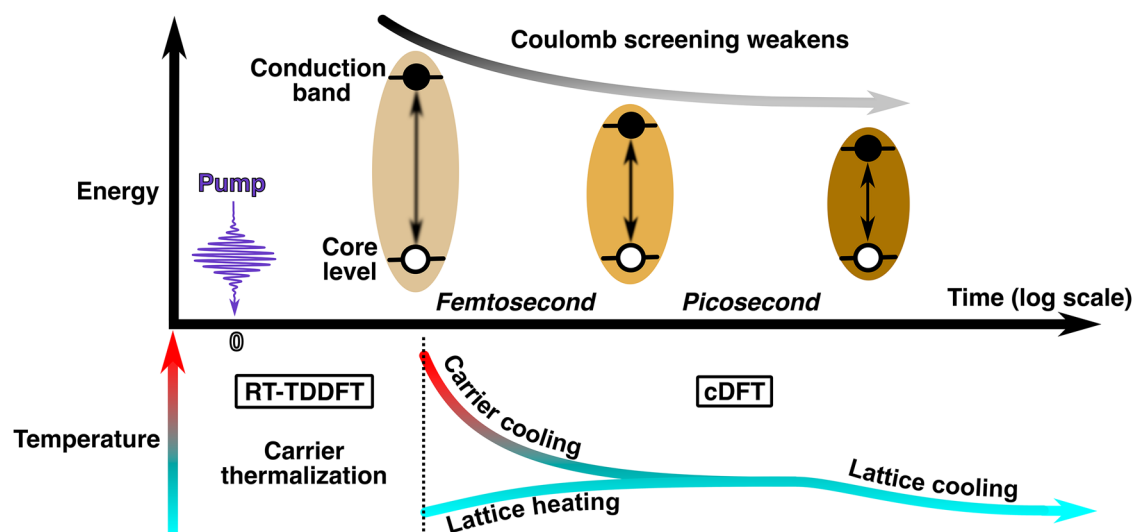


Fig. 6 | Time evolution of core-exciton screening. After pump excitation, photo-excited carriers thermalize (femtoseconds) and cool down by transferring energy to the lattice (picoseconds). The lattice gradually releases heat to the environment in a later stage (from tens of picoseconds to longer time delays). The weakening of core-

exciton screening, which reduces the energy of core-level transitions with time, is related to the dynamic changes in the density and distribution of the charge carriers. RT-TDDFT and cDFT are used to simulate the dynamics of core-exciton screening before and after carrier thermalization.

fiber/crystal laser system (Tangerine, Amplitude Systèmes) with 10 kHz repetition rate. The relative angle between the laser and the X-rays was $45 \pm 3^\circ$. Additional technical details about the measurements at the Zn K- and L-edge are provided in Supplementary section 3⁴⁰.

XTA spectra measured in fluorescence mode at the Zn K-edge are the difference between XAS spectra measured in the non-equilibrium (pumped, excited) and equilibrium (unpumped, unexcited) states, normalized by the incident X-ray intensity recorded with an ion chamber⁴¹. XTA measured in transmission at the Zn L₃-edge instead is computed from the logarithmic ratio between the pumped and unpumped spectra divided by the incident X-ray intensity. XAS and XTA spectra are normalized with respect to the edge jump for a straightforward comparison of amplitudes between experiment and theory using the Python implementation of Larch⁴². The XAS amplitude is indicated by a normalized absorption coefficient α in the figures. Additional information about data processing is provided in Supplementary section 5. Kinetic decays of XTA signals are not discussed and provided in Supplementary section 4.

Materials

The ZnO thin films measured at the Zn K-edge have a thickness of 283 ± 2 nm and are grown by pulse laser deposition on c-sapphire substrates, while the films measured at the Zn L₃-edge have a thickness of 400 ± 5 nm and are grown either by molecular beam epitaxy or radiofrequency sputtering on polycrystalline silicon nitride membranes (100 nm thickness). The (0001) orientation of the thin films was checked by X-ray diffraction, and the film thickness and optical constants were determined by spectroscopic ellipsometry. The bandgap of ZnO is 3.32 ± 0.01 eV determined by spectroscopic ellipsometry, hence the pump excitation (3.49 eV at the Zn K-edge and 3.61 eV at the Zn L₃-edge) generates electron-hole pairs above the bandgap. Sample methods and characterizations are provided in Supplementary section 2.

Computational details

All calculations were performed with the all-electron code *exciting*, where the new methodology presented in this work has been implemented. In the ground-state calculations, the Perdew-Burke-Ernzerhof functional⁴³ was employed for exchange-correlation effects. A $10 \times 10 \times 6$ k-point mesh was used to sample the first Brillouin zone. Muffin-tin radii were set to 2.0 bohr for Zn and 1.45 bohr for O, with a basis-set cut-off of $R_{MT}|\mathbf{G} + \mathbf{k}|_{\max} = 8.0$. RT-TDDFT calculations were carried out to

simulate the carrier dynamics induced by a laser pump pulse with a 10 fs FWHM duration, 3.49 eV photon energy, and an electric field along the (100) crystal axis. Local-field effects were included with $(|\mathbf{G} + \mathbf{q}|_{\max})$ set to 3.0 a.u.^{-1} . The screened Coulomb interaction was computed within the random phase approximation. A Lorentzian lineshape with a FWHM of $\delta = 1.36 \text{ eV}$ was used to account for the core-hole lifetime. The XAS spectrum was calculated by solving the Bethe-Salpeter equation using 40 unoccupied states. Scissor shifts of 141.6 eV and 37.0 eV were applied to align the computed spectra at Zn K- and L₃-edges with experimental results.

Data availability

The experimental data that support the findings of this article are available upon request from T.C.R. All input and output files of the ab initio calculations are available in the NOMAD data infrastructure with the following link: <https://doi.org/10.17172/NOMAD/2024.11.18-2>.

Received: 4 April 2025; Accepted: 28 July 2025;

Published online: 20 August 2025

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Acknowledgements

This work made use of the Pulsed Laser Deposition Shared Facility, RRID: SCR_017889, at the Materials Research Center at Northwestern University, supported by the National Science Foundation MRSEC program (DMR-2308691) and the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-2025633). RMV acknowledges funding from the Initiative and Networking Fund of the Helmholtz Association. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Numbers DE-SC0021062 (C.P.D) and DE-SC0018904 (R.F.W.). L.Q. acknowledges funding from the Alexander von Humboldt Foundation and computing time on the high-performance computer "Lise" at the NHR Center NHR@ZIB. C.Draxl appreciates funding from the DFG, projects 182087777 and 424709454. EN acknowledges DOE funding under grant DE-SC0018904 and from the Department of Defense SMART Scholarship Program. J.H.B. acknowledges support from the National Science Foundation Graduate Research Fellowship Program under Grant No. DGE21-46756. G.D. and A.M.M were supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Geosciences, and Biosciences Division under contract No. DE-AC02-06CH11357. This research used resources at the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated by the DOE Office of Science, Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

Measurements were carried out at the UE52-SGM beamline at the BESSY II electron storage ring operated by the Helmholtz Zentrum Berlin für Materialien und Energie. We thank Christian Albinus and René Grüneberger (Helmholtz Zentrum Berlin, HZB) for the 3D printing of the sample holder used in the Zn K-edge measurements, and for the design of the sample tip used in the Zn L₃-edge measurements, respectively. We thank Christopher Otolowski and Donald Walko (Argonne National Laboratory) for their support during the measurement. We thank the X-ray Corelab team at HZB for their valuable instrumental and scientific support and Yves Joly for fruitful discussions. We thank Keith Gilmore for his contributions to the implementations in the exciting code.

Author contributions

T.C.R. and L.Q. contributed equally to this work. T.C.R., L.Q., C.Draxl, and R.M.V. conceptualized the work. T.C.R., C.P.D., R.F.W., J.H.B., E.N., A.M.M., and G.D. conducted the experiment at the Zn K-edge. T.C.R., C.P.D., R.G., and M.F. conducted the experiment at the Zn L₃-edge. L.Q. performed the ab initio calculations. R.R.P. implemented the cDFT and RT-TDDFT methods. D.B.B., C.Deparis, J.Z.P., M.W., and K.E. synthesized the samples. T.C.R., L.Q., C.Draxl, and R.M.V. wrote the manuscript with input contributions from every author.

Funding

Open Access funding enabled and organized by Projekt DEAL.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s43246-025-00909-w>.

Correspondence and requests for materials should be addressed to Thomas C. Rossi or Lu Qiao.

Peer review information *Communications Materials* thanks the anonymous reviewers for their contribution to the peer review of this work. Primary Handling Editors: Kai-Qiang Lin and Aldo Isidori. A peer review file is available.

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¹Department of Atomic-Scale Dynamics in Light-Energy Conversion (PS-ADLU), Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany.

²Department of Physics and CSMB, Humboldt-Universität zu Berlin, Berlin, Germany. ³Department of Chemistry, University of Illinois Urbana-Champaign, Urbana, IL, USA. ⁴Supercomputing Department, Zuse Institute Berlin (ZIB), Berlin, Germany. ⁵Combined X-ray methods at BLIX and BESSY II - SyncLab, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany. ⁶Institute for Physics and Astronomy, Technische Universität Berlin, Berlin, Germany. ⁷Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA. ⁸Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA. ⁹Université Côte d'Azur, CNRS, CRHEA, Valbonne, France. ¹⁰Majulab, International Research Laboratory IRL 3654, CNRS, Université Côte d'Azur, Sorbonne Université, National University of Singapore, Nanyang Technological University, Singapore, Singapore. ¹¹Optotransmitter-Umweltschutz-Technologie (OUT) e.V., Berlin, Germany. ¹²Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Methods and Instrumentation for Synchrotron Radiation Research, Berlin, Germany. ¹³These authors contributed equally: Thomas C. Rossi, Lu Qiao. ✉e-mail: thomas.rossi@helmholtz-berlin.de; qiaolu@physik.hu-berlin.de