Clocking the Ultrafast Electron Cooling in Anatase Titanium Dioxide Nanoparticles

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Supporting Information

ABSTRACT: The recent identification of strongly bound excitons in room-temperature anatase TiO₂ single crystals and nanoparticles underscores the importance of bulk many-body effects in samples used for applications. Here, for the first time, we unravel the interplay between many-body interactions and correlations in highly excited anatase TiO₂ nanoparticles using ultrafast two-dimensional deep-ultraviolet spectroscopy. With this approach, under nonresonant excitation, we disentangle the optical nonlinearities contributing to the bleach of the lowest direct exciton peak. This allows us to clock the ultrafast time scale of the hot electron thermalization in the conduction band with unprecedented temporal resolution, which we determine to be <50 fs, due to the strong electron–phonon coupling in the material. Our findings call for the design of alternative resonant excitation schemes in photonics and nanotechnology.

KEYWORDS: titanium dioxide, ultrafast dynamics, electron cooling, two-dimensional spectroscopy, nanoparticles, exciton optical nonlinearities

In the last decades, anatase TiO₂ has attracted huge interest as one of the most promising materials for a variety of challenging applications, ranging from photocatalysis and photovoltaics to sensors. Since these technologies involve charge transport, thermalization, and localization, they call for studies of the electron and hole dynamics, which provide a deep knowledge of the nature of the photogenerated/injected charge carriers and of the energy balance therein. These processes intimately depend on the details of the electronic structure and the presence of many-body effects in the material. Since anatase TiO₂ is a d⁰ transition metal oxide, strong electron–electron correlations do not play a substantial role in the electronic structure. Hence, this solid can be classified within the simple band insulator scheme, in which the forbidden energy gap arises as a result of band theory and is not a consequence of the strong on-site Coulomb interaction. However, different from conventional band insulators, anatase TiO₂ represents a peculiar example in which electron–phonon interaction and electron–hole correlation become relatively strong and influence the optical spectra. On the one hand, the presence of a moderately large electron–phonon coupling in anatase TiO₂ has often been invoked to interpret experimental results naturally pointing to the polaronic (self-trapped) picture. Notable examples include the low-temperature green photoluminescence (PL) due to self-trapped excitons and the room-temperature electron mobilities whose values are limited by strong scattering with phonons. On the other hand, many-body correlations have been thought to be negligible in this material, and, as such, they remained widely unexplored. Recently, by employing state-of-the-art experimental and computational techniques, the substantial role of electron–hole Coulomb correlations was unravelled in the anatase polymorph of TiO₂. Strongly bound direct excitons were found to emerge with a binding energy exceeding 150 meV and a pronounced coupling to the phonon degrees of freedom. As a result, these excitons are notably very robust with respect to temperature and sample quality, clearly appearing in single crystals with various degrees of doping and in defect-rich samples, such as nanoparticles (NPs) with typical radii of 5–15 nm. The latter are representative of the quality of anatase TiO₂ used in room-temperature applications.

Given the importance of interactions and correlations in anatase TiO₂, one expects them to have a pronounced influence on the carrier dynamics. In particular, these phenomena are predicted to govern the time scales for intraband carrier cooling via phonon emission, and they can also influence the optical properties of the material via strong optical nonlinearities. As such, their understanding is of pivotal importance for the design of novel devices and the optimization of existing ones.

So far, the charge carrier dynamics in TiO₂ has intensely been studied by ultrafast broadband transient absorption (TA) spectroscopy from the terahertz to the visible. In these studies, the photoexcited electrons and holes in the system were treated as uncorrelated, an approximation that is valid only when the pump photons are nonresonant with the excitons. Under these conditions, the material response is dominated by a free-carrier Drude response and by absorption

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features attributed to localized charges trapped at impurity and/or defect centers. Although these studies shed light on the electron–hole recombination pathways, they were biased toward surface effects, probed only intraband transitions, and ignored the material electronic structure, while the identification of impurity/defect bands is still debated. More insightful information was provided by time-resolved PL, which revealed a strongly Stokes-shifted emission in the visible range assigned to self-trapped excitons and/or charges trapped at defects. However, these processes were found to emerge only at low temperatures and to disappear at room temperature. Furthermore, only long time scales (>20 ps) were investigated.

To detect possible signatures of interactions and correlations in the dynamical response of anatase TiO$_2$, one needs a TA method that combines a sub-100 fs temporal resolution with both excitation and probing over a broad spectral window in the deep-ultraviolet (UV). It would allow direct access to the region in which spectral weight is removed after above-gap excitation and excitonic features become clearly distinguishable. Insightful information on single-particle and many-body effects is encoded in the bleaching of the exciton state, a nonlinear optical effect that depends on the presence of all the particles (i.e., electrons, holes, ...) in the material. Such a method has recently become possible as two-dimensional (2D) deep-UV TA spectroscopy.

When dealing with excitonic optical nonlinearities in semiconductors, the most prominent effects are (i) phase-space filling (PSF), which causes a reduced oscillator strength by decreasing the number of single-particle states contributing to the exciton; (ii) long-range Coulomb screening (CS), which broadens the exciton band and shifts it to the blue, as the photoexcited carrier density screens the electron–hole interaction and reduces the exciton binding energy; and (iii) band-gap renormalization (BGR), which leads to a density-dependent shrinkage of the single-particle states (and consequently of the exciton states) and may reduce the exciton oscillator strength. These processes act simultaneously on the exciton line shapes, their relative weights being governed by the material parameters and dimensionality.

Here, using ultrafast 2D deep-UV spectroscopy, we reveal the hierarchy of exciton nonlinearities in anatase TiO$_2$ NPs excited above the band gap. We find that PSF of the conduction band (CB) by the photoexcited electron density represents the main mechanism upon light generation of uncorrelated electron–hole pairs. This allows us to address the long elusive question of the time scales involved in the intraband hot electron thermalization in anatase TiO$_2$. Specifically, we find an ultrafast electron cooling within 50 fs, which is compatible with phonon-mediated relaxation processes in the strong coupling regime.

The experimental procedures are described in Sections S1 and S2 in the Supporting Information (SI). In a first experiment, we vary the pump between 4.00 and 4.60 eV and monitor the TA signal, $\Delta A$, over a broad spectral range covering the excitonic resonances (3.50–4.60 eV). The time resolution is 150 fs, and the photoexcited carrier density is $n = 5.7 \times 10^{19}$ cm$^{-3}$. This high-excitation density regime is chosen to ensure that the excitonic absorption is fully saturated.
to avoid polaronic effects within the bands and promote the formation of a mobile electron–hole liquid.12 Figure 1(a) shows ultrafast 2D deep-UV pump–probe color-coded maps at different time delays (1, 100, and 500 ps). The straight line in each map indicates the region in which pump and probe have the same photon energy, and it is affected by artifacts due to the scattering of the pump beam into the spectrometer. All transients are characterized by a negative signal over the entire probe spectral range, in which two long-lived features are clearly distinguished at probe photon energies of 3.88 and 4.35 eV. While the former is present at all pump photon energies, the latter becomes more prominent when the pump is tuned above 4.10 eV. Cuts of the 1 ps map at specific probe photon energies are shown in Figure 1(b), normalized to the maximum amplitude of the 3.88 eV feature. They are compared to the inverted steady-state absorption spectrum ($\sim$300 meV. These bands are hidden in the steady-state absorption spectrum due to the strong scattering of light, but become apparent in the TA spectrum due to cancellation of the probe scattered light in the difference spectrum. Moreover, the peak of the low-energy Lorentzian band is independent of the pump photon energy, while clear information on the high-energy feature cannot be retrieved due to the influence of the pump beam scattering. We recently identified the features at 3.88 and ~4.35 eV as bound excitons along the a- and c-axes of single crystals of anatase TiO$_2$.13 They show up in Figure 1 due to the random orientation of NPs in solution, underscoring the analogy of the spectroscopic features of NPs and bulk single crystals.

From Figure 1 we can already draw an important conclusion on the nonequilibrium dynamics of anatase TiO$_2$ NPs, which was neglected in previous studies. Depending on the choice of the pump photon energy, one can create uncorrelated electron–hole pairs (nonresonant excitation) or excitons (resonant excitation). In the former case, the pump photon energy determines the regions of the Brillouin zone where the nonequilibrium electron–hole density is created. This consideration is of importance in the case of an indirect band-gap insulator such as anatase TiO$_2$, since the pump photon energy can also be tuned to phonon-assisted interband transitions (despite their lower cross section). On the contrary, resonant excitation leads to the creation of bound exciton species in the system, which complicates the interpretation of the ultrafast dynamics due to the presence of many-body exciton–exciton interactions. This case will be addressed in future work, while here we focus on the nonresonant excitation and clarify the impact of uncorrelated electron–hole pairs on the bound exciton spectral feature. To this purpose, we select a data set from Figure 1, namely, the one at the pump photon energy of 4.05 eV, since it lies above the a-axis and below the c-axis exciton peak and is expected to minimize their contribution. This, in turn, allows us to link more accurately the resulting ultrafast dynamics to the details of the electronic structure. The data are displayed in Figure 2(a) as a color-coded map of $\Delta A$ as a function of probe photon energy and time delay between pump and probe. As expected, the spectral response features the long-lived a-axis exciton band at 3.88 eV, followed by the weaker shoulder of the c-axis exciton around 4.35 eV. The transient spectra at different time delays of Figure 2(b) show that the 3.88 eV band does not change with time (Figure S2). Figure 2(c) displays the kinetic traces at three specific probe photon energies: below (3.77 eV), at (3.90 eV), and above (4.10 eV) the a-axis exciton peak. All temporal traces exhibit a resolution-limited rise of 150 fs, followed by a long-lived decay persisting beyond 1 ns. In addition, a low-frequency oscillation modulates the whole spectrum during the first 5 ps, which is fully damped within one oscillation. This feature is due to

Figure 2. (a) Color-coded map of $\Delta A$ measured on a colloidal solution of anatase TiO$_2$ NPs as a function of probe photon energy and time delay between pump and probe. The time resolution is estimated to be 150 fs, the pump photon energy is set at 4.05 eV, and the photoexcited carrier density is $n = 5.7 \times 10^{19}$ cm$^{-3}$. (b) $\Delta A$ spectra as a function of probe photon energy at representative delay times between pump and probe. (c) Experimental temporal traces of $\Delta A$ for different probe photon energies (dotted lines) and results of the global fit analysis (solid lines). (d) Contribution to the $\Delta A$ response of the four relaxation components obtained from the global fit analysis.
coherent acoustic phonons confined within the spherical TiO$_2$ NPs, and it will be discussed elsewhere. Here, we retrieve the significant parameters of the incoherent response, by performing a global fit of 16 selected temporal traces in the 3.60–4.40 eV probe range of the $\Delta A$ map. A satisfactory global fit up to 1 ns (solid line in Figure 2(c)) is optimal using a multi-exponential function with four time constants ($\tau$) convoluted with a Gaussian accounting for the instrument response function (IRF) of $\sim$150 fs: $\tau_1 = 1.60 \pm 0.12$ ps, $\tau_2 = 10 \pm 0.40$ ps, $\tau_3 = 50 \pm 1.70$ ps, $\tau_4 = 423 \pm 14.70$ ps. The global fit enables us to disentangle the spectral dependence of the decay processes contributing to the recovery of the exciton bleach. To this aim, in Figure 2(d), we plot the pre-exponential factors associated with a given time constant as a function of the probe photon energy. The spectral dependence of the $\tau_1$ and $\tau_2$ components shows a negative amplitude broader than the exciton line shapes, while the contributions of the $\tau_3$ and $\tau_4$ components mainly reproduce the contours of both exciton bands, suggestive of a different nature for the two sets of components. All decay processes are strictly related to the electron–hole recombination mechanisms, which reduce the density of delocalized carriers via radiative or nonradiative relaxation channels.

In order to identify the phenomena behind the different time constants, one first needs to assess the relative weights of the optical nonlinearities contributing to the transient signal. Central for this is to clarify the electron–hole populations giving rise to the exciton collective state. Based on the band structure of anatase TiO$_2$, the single-particle states contributing to the a-axis exciton lie along the $\Gamma$–$Z$ direction of the Brillouin zone (Figure 3). Due to the symmetry of the p–d wave functions, however, the states exactly at the $\Gamma$ point are symmetry forbidden and do not contribute to the exciton state. Once a nonequilibrium distribution of uncorrelated electron–hole pairs is created, the electrons are expected to thermalize to the bottom of the CB at $\Gamma$ and the holes to the top of the valence band (VB) close to X. Since the deep-UV probe is sensitive to the joint density of states in the material, an induced transparency ($\Delta A < 0$) can arise from a density of electrons (holes) accumulated in the CB (VB) alone. In anatase TiO$_2$, the PSF contribution to the exciton bleaching is expected to arise exclusively due to an electron population close to the bottom of the CB. The hole contribution is absent, due to their ultimate relaxation to the top of the VB close to the X point. Consistent with this scenario, the exciton bleach is found to persist even when the pump photon energy is tuned to 3.54 eV, thus promoting indirect (phonon-assisted) interband transitions. On the contrary, upon 3.10 eV excitation, no signal is detected even up to incident fluences of 34 mJ/cm$^2$.

The above considerations imply that PSF, long-range CS, and BGR all may contribute to the observed optical nonlinearities. This requires addressing the effects related to the enhancement of the electronic screening upon pump photoexcitation. To this aim, we study how the exciton spectrum is renormalized as a function of the pump fluence at 4.05 eV, narrowing our detection range to cover only the spectral region of the a-axis exciton. This allows a higher stability of our setup, maintaining the same experimental conditions over the time required for the fluence dependence study. Within the explored range, the maximum intensity of the signal scales linearly with the absorbed fluence (Figure S3), which excludes multiphoton absorption processes from the pump beam. The normalized spectra are shown in Figure 4(a,b) for delay times of 400 fs and 10 ps, respectively. We observe that the exciton line shape slightly broadens with increasing carrier density. We assign this behavior to the presence of long-range CS. Indeed, under our experimental conditions, we can exclude that the broadening originates from other exciton decay channels opened by the photoexcitation process. Radiative or nonradiative exciton decay processes are found in direct band-gap semiconductors in the presence of low-dimensionality and reduced dielectric screening, since nonresonant photoexcitation can spontaneously evolve into exciton formation via the single-particle states at the band edges. In contrast, in indirect band-gap semiconductors, photoexcited uncorrelated electrons and holes quickly relax toward the bottom of their respective bands and no direct excitons are energetically favored. In principle, indirect excitons would be allowed to form through the mediation of phonon modes. However, in the case of anatase TiO$_2$ nanosystems, their existence at room temperature has been disproven by extensive measurements and by the results we present in the following. As such, many-body processes such as exciton–exciton annihilation can be excluded. Consistent with the idea that long-range CS from free carriers is the optical nonlinearity governing the exciton broadening, in a recent study we found that the excitonic band of anatase TiO$_2$ is broadened upon charge injection from an external dye adsorbed on the surface of NPs (i.e., in the absence of holes in the VB of TiO$_2$). Long-range CS is also expected to lead to a blue-shift of the exciton peak. However, within our experimental accuracy, here we observe no shifts in the peak energy position nor derivative-like shapes. This apparent insensitivity of the exciton peak energy to the photoinduced carrier density even in the presence of CS-induced broadening has been rationalized in the literature as an exact cancellation of the effects of CS and BGR on the excitonic resonances at all densities. In general, the quantitative details of this compensation depend on both material and dimensionality. From these measurements, we can conclude that the carrier density that is required to induce dramatic changes of the

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**Figure 3.** Schematic representation of the deep-UV based detection of the ultrafast carrier dynamics in anatase TiO$_2$ NPs. The pump photon at 4.05 eV (purple arrow) excites electron–hole pairs through direct transitions. The broadband UV pulse (violet arrows) probes the exciton feature at 3.88 eV. The direct transitions contributing to this collective state lie along the $\Gamma$–$Z$ region of the Brillouin zone. The band structure of anatase TiO$_2$ has been adapted from ref 23.
exciton peak energy is higher than those produced by our photoexcitation. As a consequence, at sufficiently low electron–hole pair densities, when the continuum is still far from the resonances, only the loss of oscillator strength due to PSF and a slight broadening due to CS are apparent.

Having established the dominant role played by CB electrons in blocking the excitonic transitions allows one to retrieve valuable information on the electron recombination dynamics. Indeed, the $\Delta A$ signal at the excitonic resonance can be used as a measure of the photoexcited electron concentration changing with time. Representative temporal traces at a probe photon energy of 3.88 eV and for different excitation densities are shown in Figure 4(c) and normalized with respect to their maximum. We observe that below 40 ps the bleach recovery accelerates with fluence, which is indicative of higher-order recombination processes for the charge carriers, such as bimolecular and Auger recombination. Indeed, the recombination dynamics in semiconductors and insulators proceeds via single-carrier nonradiative processes (trapping at impurity states), two-body radiative (bimolecular) mechanisms, and nonradiative trap–Auger recombination processes and three-body band-to-band Auger processes. Since anatase TiO$_2$ is an indirect band-gap insulator, band-to-band radiative processes in the infrared and the visible ranges for highly excited anatase TiO$_2$ NPs and thin films. It is also consistent with the spectral dependence of the $\tau_1$ and $\tau_2$ relaxation components (Figure 2(d)), whose broad shape hints at energetically redistributed carriers over a wider phase space during the Auger processes. In contrast, the longer $\tau_1$ and $\tau_2$ relaxation components can be assigned to electron trapping processes at defect states, which lead to bleach recovery by emptying the phase space involved in the exciton state.

More interestingly, having established PSF as the main mechanism behind exciton bleaching allows us to address the long elusive issue of the time scale of electron cooling to the CB minimum in anatase TiO$_2$. A recent single-wavelength transient reflectivity experiment on rutile TiO$_2$ single crystals tracked the influence of carrier cooling onto the phase of the coherent $A_g$ phonon mode at 74.4 meV, offering valuable information on the electron–phonon coupling dynamics. Nevertheless, this approach is blind to the details of the electronic structure and relies on the analysis of coherent optical phonons, whose observation is not always straightforward.

Here, we circumvent these limitations by demonstrating the effectiveness of exciton bleaching as a probe of the intraband electron thermalization. To this aim, we focus on the rise of the exciton bleach signal by reducing the IRF of our setup to 80 fs

Figure 4. (a, b) Normalized $\Delta A$ spectra as a function of probe photon energy for different photoexcited carrier densities. Spectra in (a) are cut at a delay time of 400 fs; spectra in (b) at 10 ps. (c) Normalized temporal traces at 3.88 eV for different photoexcited carrier densities.

Figure 5. (a) Experimental spectrum of the ultrafast PL at a time delay of 1 ps (violet curve) and Gaussian fit of the response (blue curve). (b) Temporal evolution of the ultrafast PL at 1.91 eV (red dots), 2.18 eV (blue dots), and 2.58 eV (violet dots). The solid lines are fit to the experimental curves.
(see Methods in the SI). In Figure 6(a), we compare the signal at 3.88 eV and an excitation density $n \approx 2.1 \times 10^{19}$ cm$^{-3}$ (violet curve) with that of the pure solvent (pink curve). In both traces, artifacts due to residual cross-phase modulation (CPM) after $t = 0$ can be identified. Moreover, while the signal from the solvent dies immediately after the CPM, the one from anatase TiO$_2$ persists over time and comprises a relaxation component that starts around 200 fs. However, to isolate the anatase TiO$_2$ signal, the two traces cannot be directly subtracted due to slightly different experimental conditions in the measurements. Therefore, we adopt a common procedure in ultrafast spectroscopy, in which the IRF is assumed to coincide with the duration of the CPM signal and is represented by a Gaussian function (with a full-width at half-maximum of 80 fs) folding in the CPM modulations (blue curve in Figure 6(a)). The isolated TiO$_2$ signal is shown as red dots superimposed to the original trace. To provide an upper limit to the rise time of the bleach signal, in Figure 6(b) the isolated TiO$_2$ signal (red dots) is compared to three computed time traces convoluted with the Gaussian IRF of 80 fs. They consist of different rise times and an exponential computed recovery time of 200 fs. Here, the time $t = 0$ is consistently defined with respect to the subtracted CPM. It can be seen that the 20 fs rise time interpolates nicely between the $t < 0$ points and the $t > 200$ fs ones. In any case, the upper limit cannot exceed 50 fs. Thus, the rise of the exciton bleach is <50 fs, which is the time scale for the intraband electron cooling.

We now discuss the origin of this ultrafast electron cooling. Upon photoexcitation, momentum conservation results in the partition of the excess energy provided by the pump pulse into kinetic energy of the electrons and holes according to the reciprocal ratio of their effective mass $m_{e}^*/m_{h}^*$, with the carrier having a lower effective mass receiving more excess energy:

$$E_{\text{exc}}^e (\hbar \omega) = \frac{\hbar^2 k^2}{2m_e} = \frac{m_{h}^*}{m_{e}^* + m_h^*}(\hbar \omega - E_{\text{gap}})$$  \hspace{1cm} (1)

$$E_{\text{exc}}^h (\hbar \omega) = \frac{\hbar^2 k^2}{2m_h} = \frac{m_{h}^*}{m_{e}^* + m_h^*}(\hbar \omega - E_{\text{gap}})$$  \hspace{1cm} (2)

In our experiment, $\hbar \omega = 4.05$ eV and $E_{\text{gap}} = 3.20$ eV. Rigorously, the electron and hole effective masses vary as a function of momentum $k$. These masses are well-defined concepts only within the parabolic approximation for the band structure. From the latter, we expect our pump photons to promote uncorrelated electron–hole pairs in the vicinity of the $\Gamma$ point along the $\Gamma$–X direction (purple arrow in Figure 3).

Due to the high carrier densities involved in our experiment, we use the value of the electron effective mass reported by band theory $m^*_e = 0.42 m_e$ (see Section S5 for the choice of $m^*_e$). Performing a parabolic fit yields $m^*_h = (2.78 \pm 0.5) m_h$, which also accounts for the polaronic contribution to the mass renormalization. The values of $m^*_e$ and $m^*_h$ lead to the excess energy partition $E_{\text{exc}}^e \approx 0.74$ eV and $E_{\text{exc}}^h \approx 0.11$ eV.

Once the carriers have received this excess energy in their respective bands, they start interacting with the phonon modes of the lattice. When the time scale obtained for the electron cooling in anatase TiO$_2$ is compared with the slower (>250 fs) electron relaxation time scales retrieved in nonpolar indirect gap semiconductors, some conclusions can be drawn concerning the role of electron–phonon scattering in different materials. In nonpolar semiconductors (such as Ge and Si) phonon scattering occurs through the optical phonon deformation potential interaction, while in partially ionic polar systems (such as anatase TiO$_2$) the most effective coupling mechanism is represented by the electron–longitudinal optical (LO) phonon scattering described by the Fröhlich interaction. In TiO$_2$, the optical phonons that are most strongly coupled to the electronic degrees of freedom are those belonging to the bands of $E_m$ and $A_{2u}$ modes. Due to this coupling, in the low carrier density limit, the CB electrons form well-defined large polaron quasiparticles, characterized by a dimensionless polaron coupling constant $\alpha \approx 2$. This constant determines the ratio between the polaron self-energy and the LO phonon energy, thus defining an intermediate to strong electron–phonon coupling regime for the electrons in anatase TiO$_2$. At high density, the polaronic quasiparticle is observed to collapse into an electron liquid coupled to the phonon modes. Within the single-particle limit probed by ARPES, the crossover takes place around $n = 10^{19}$
cm. In the two-particle limit of optical absorption, this threshold may be even lower, leading to the emergence of a well-defined Drude response for the photocarriers instead of the characteristic absorption features of large polarons. Even in this diffusive regime, the electron–phonon coupling can lead to an efficient and fast transfer of electron excess energies to the phonon bath within a few tens of fs.

To theoretically interpret the relaxation times observed in our experiment, we first rely on a simple estimate of the scattering rate as expected from first-order perturbation theory. In the case of electrons in a parabolic CB, the scattering rate can be calculated via Fermi’s golden rule as

$$\Gamma = \Gamma_0 \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_i} \right) \text{arcsinh} \left( \frac{E_{\text{exc}}}{\hbar \omega_{\text{LO}}} - 1 \right) \left( 1 + 2n_{\text{BE}} \right)$$  \hspace{1cm} (3)

where $\epsilon_\infty$ and $\epsilon_i$ are the dielectric constants at energies well above and below the phonon energy $\hbar \omega_{\text{LO}}$, respectively, and $n_{\text{BE}}$ is the Bose–Einstein statistical factor. $\Gamma_0$ is a nearly temperature-independent prefactor that reads

$$\Gamma_0 = \sqrt{\frac{m^*_e \epsilon_\infty^2 \epsilon_i \omega_{\text{LO}}}{2E_{\text{exc}} 2\pi \hbar \epsilon_0}}$$  \hspace{1cm} (4)

Substituting the relevant parameters for anatase TiO$_2$, yields $\sim$4 fs for the electron cooling time, which could be compatible with our experimental observation. However, we point out that eq 3 is valid under the conditions that a single phonon mode is interacting with the electrons and that $\alpha < 1$. Since $\alpha$ represents a measure for the relative importance of higher-order processes, eq 3 may not provide an accurate estimate of the actual electron cooling rate. A more reliable estimate relies on density-functional perturbation theory accounting for the phonon density of states of the material, as computed in ref 13.

According to this ab initio approach, under our experimental conditions we expect the time scale for emission of a single phonon by an excited electron to be $\sim$2 fs and the total thermalization time to the CB edge $\sim$40 fs, in very good agreement with the present upper limit of 50 fs (Figure 3). On the other hand, the holes can undergo rapid intervalley scattering to the X and Z points via emission of high-wavevector phonons.

Within the semiclassical limit, for excess energies less than the minimum LO phonon energy ($\sim$45 meV in TiO$_2$), severe constraints in the phonon phase space are expected to result in a dramatic decrease of the intraband cooling rate. However, for polaronic materials governed by the Fröhlich interaction, purely quantum kinetic relaxation channels can open also in the case of small excess energies, leading to an efficient redistribution of the electronic energy into the strongly coupled phonons. This effect can be viewed as the buildup of the polaronic dressing in the low-density limit. Future quantum kinetic calculations involving the solution of the Dyson equation will shed light on these phenomena. At this stage, irrespective of the mechanism at play, the net result is that no effective energy will be stored in the electronic degrees of freedom for sufficiently long time scales.

These arguments lead us to conclude that, in anatase TiO$_2$, fast relaxation processes impose serious limitations on the practical use of the full photon energy in applications. This scenario is radically different from the physics of semiconductor quantum dots, in which the spacing between the discrete electronic levels is large enough to prevent fast phonon-mediated carrier cooling processes. For photocatalysis, fast thermalization is a favorable process, since the lower energy states are important. This issue is also of importance in photovoltaics since a large driving force is often sought after for efficient injection, especially when the coupling between the sensitizer to the TiO$_2$ substrate is weak. However, the present study shows that the large excess energy is lost to phonons. Therefore, alternative excitation schemes, such as resonant excitation of the strongly bound exciton species, are preferable in which the energy can be temporally harvested. Another ideal situation is illustrated by the simulations by de Angelis et al., showing a strong hybridization of the wave functions of the sensitizer and the substrate. Furthermore, as we showed that the a-axis excitons are 2D and robust against temperature and defects, they are expected to move freely on the (001) plane.

As such, they may offer an efficient source to mediate the flow of energy at the nanoscale in engineered devices based on anatase TiO$_2$.

In summary, we have provided direct evidence of excitonic optical nonlinearities in anatase TiO$_2$ nanoparticles at room temperature. Besides their fundamental importance, these excitons hold huge promise for future technological developments, in particular in the emerging field of excitonics. We revealed selective information on the intraband and interband electron dynamics by tracking the renormalization of the excitonic features over time. We showed that in nanosized anatase TiO$_2$ the strong electron–phonon coupling of the material results in very fast cooling times for electrons possessing a substantial (>0.2 eV) excess energy. Under these conditions, any optical or acoustic phonon can be excited in the course of the electron thermalization, thus contributing to a rapid loss of the electronic excess energy, making it ineffective in devices based on anatase TiO$_2$. More remarkably, our results highlight the importance of relating the carrier dynamics of anatase TiO$_2$ NPs to the details of the electronic structure, an aspect that was overlooked in all previous experimental studies. Finally, by unraveling the origin of the bound exciton bleaching in NPs, our findings pave the way to its use as a sensor of carrier dynamics in a variety of nanosystems based on anatase TiO$_2$. Notable examples include modified forms of this material, such as the ones obtained upon chemical doping with magnetic ions or upon crystal structure control.

**ASSOCIATED CONTENT**

Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.7b00945.

Materials and methods, additional results, and references (PDF)

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