Phonon-Driven Selective Modulation of Exciton Oscillator Strengths in Anatase TiO$_2$ Nanoparticles

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Supporting Information

ABSTRACT: The way nuclear motion affects electronic responses has become a very hot topic in materials science. Coherent acoustic phonons can dynamically modify optical, magnetic, and mechanical properties at ultrasonic frequencies, with promising applications as sensors and transducers. Here, by means of ultrafast broadband deep-ultraviolet spectroscopy, we demonstrate that coherent acoustic phonons confined in anatase TiO$_2$ nanoparticles can selectively modulate the oscillator strength of the two-dimensional bound excitons supported by the material. We use many-body perturbation-theory calculations to reveal that the deformation potential is the mechanism behind the generation of the observed coherent acoustic wavepackets. Our results offer a route to manipulate and dynamically tune the properties of excitons in the deep-ultraviolet at room temperature.

KEYWORDS: Ultrafast spectroscopy, excitons, coherent acoustic phonons, anatase TiO$_2$, deep-ultraviolet, nanoparticles

The field of excitonics is attracting increasing interest for storing, guiding, and manipulating light at the nanoscale via collective bound states of electron–hole pairs. As such, one of the primary goals of research is to reach high control and tunability of the exciton optical properties (i.e., line width, energy, oscillator strength) in distinct spectral ranges through different external perturbations. Typical examples of control parameters include temperature, pressure, electric/magnetic field, mechanical stress and photoexcitation.1–3 On the one hand, varying the exciton peak energy is highly desirable for ensuring wavelength tunability to exciton radiative recombination in direct gap semiconductors or for discriminating between degenerate exciton states in valleytronic materials.1–6 On the other hand, modifying the exciton oscillator strength has led to considerable developments in low-power all-optical switching and signal processing, with the photoinduced saturation of the excitonic absorption being the most significant one.7

A novel frontier in the field involves pushing these effects to a coherent regime through the use of tailored ultrashort laser pulses, realizing a time-periodic modulation of the exciton optical properties.8 Recently, huge efforts have been devoted to dynamically modulate the peak energy of excitons.9–13 A promising framework is based on the optical Stark effect, in which off-resonant (i.e., below gap) photons dress the excitonic states of a material within the strong coupling regime. With this method, remarkable exciton shifts of 10–18 meV have been obtained in monolayer transition metal dichalcogenides at room temperature.9,10 An alternative approach relies on tuning the exciton energy by photoinducing a time-dependent ionic motion. In this scenario, exciton shifts as large as 10 meV have been demonstrated in semiconductor nanostructures, although at very low temperatures.11,12 Experiments at room temperature are rarer, due to the scarcity of materials in which excitons can still emerge as robust quasiparticles and coherent phonons are not suppressed by fast thermal dephasing. A prototypical example is offered by quantum dots, where the exciton–phonon coupling is enhanced by their low dimensionality, leading to exciton shifts of several millielectronvolts.13 However, so far, achieving the selective modulation of an exciton oscillator strength has remained a challenge. In this scenario, only the exciton peak amplitude is expected to periodically react to the external coherent perturbation, while
the resonance energy remains anchored to its equilibrium value. To our knowledge, this effect has only been reported for charge-transfer excitons of specific molecular systems, with no direct counterparts in solids. Reaching a coherent amplitude modulation of an exciton resonance would allow a range of potential applications, as the exciton oscillator strength can act as a sensor of the external acoustic field.

In this Letter, we demonstrate the phonon-driven selective modulation of the exciton oscillator strength in the technologically relevant oxide anatase TiO$_2$. This semiconductor crystallizes in a tetragonal unit cell built on a network of corner- or edge-sharing TiO$_6$ octahedra, with a strong anisotropy between the lattice constants $a = 3.78$ Å and $c = 9.51$ Å. In its nanosized form, it is widely recognized as a superior system for several applications, ranging from photocatalysis to dye-sensitized solar cells and sensors. In a previous work, we demonstrated that pronounced electron–hole correlations govern the deep-ultraviolet (UV) optical properties of this material, giving rise to strongly bound excitons with a binding energy exceeding 150 meV. The lowest-energy ($a$-axis) exciton is dipole-allowed when the light polarization lies along the (001) crystallographic plane, and possesses a two-dimensional wave function in the three-dimensional crystal lattice (Figure 1a). The highest-energy ($c$-axis) exciton is active for light polarized along the [001] axis, and is characterized by a localized and almost spherical wave function (Figure 1b). With respect to these bound states, conventional nanosystems such as TiO$_2$ nanoparticles (NPs) with diameters >5 nm behave similarly to the bulk, as they are larger than the exciton Bohr radius (3.2 nm). In addition, excitons are notably very robust against temperature and sample quality, clearly appearing in the defect-rich NPs and films used in room temperature applications. Importantly, these excitons also possess a strong coupling to the lattice degrees of freedom, making them ideal candidates to test schemes of dynamical manipulation based on a photoinduced ionic motion. In this respect, nanosized systems offer a high degree of flexibility with regard to coherent acoustic phonons, as the latter become confined entities when the phonon coherence length is comparable to the size of the system. Under these conditions, different geometries of the nano-objects lead to a discrete set of eigenmodes that can be tested for ultrafast exciton control.

Here, we use an ultrashort deep-UV laser pulse to impulsively launch confined coherent acoustic phonons inside spherical anatase TiO$_2$ NPs. By means of ultrafast broadband deep-UV spectroscopy, we observe that the resulting mechanical motion of the NPs induces a giant coherent modulation of the two-dimensional exciton oscillator strength, without affecting the peak energy of the resonance. To rationalize the generation mechanism of the coherent strain pulses, we combine our results with advanced many-body perturbation theory calculations. These findings shed light on strong exciton–phonon coupling phenomena in nanosized anatase TiO$_2$ and pave the way to exploiting the material’s two-dimensional exciton as a promising basis for new pressure sensors.
Anatase TiO$_2$ NPs with an average diameter of 25 nm were prepared using the sol–gel method,$^{28}$ dispersed in a colloidal solution and circulated into a quartz flow-cell at room temperature. For the ultrafast broadband deep-UV experiments, we used the setup described in ref.$^{29}$ Specifically, we used a deep-UV laser pulse to photoexcite the NPs, setting its photon energy above the $a$-axis exciton peak (4.05 eV). As a result, uncorrelated electron–hole pairs are generated. Subsequently, the relative changes in the NPs absorption ($\Delta A$) were monitored over a broad spectral range covering the exciton feature (3.40–4.50 eV). The time resolution was 150 fs. Many-body perturbation theory at the GW level$^{30,31}$ was employed to compute the band structure of the material for an unstrained unit cell and in the presence of hydrostatic pressure. More details are provided in the Methods.

Figure 2a displays the color map of $\Delta A$ as a function of probe photon energy and time delay between pump and probe. The photoexcited carrier density was $n \sim 5.7 \times 10^{19}$ cm$^{-3}$. Although the signal was measured up to 1 ns, the map purposely zooms into the first 15 ps. The signal is characterized by a negative response over the entire probe range, and it exhibits two long-lived features around 3.88 and 4.35 eV. These structures correspond to the $a$- and $c$-axis bound excitons, respectively,$^{19}$ which are bleached as a result of above-gap photoexcitation (as discussed in detail in ref 32). Contrary to the transient reflectivity measurements in single crystals,$^{19}$ both excitons are observed in the ultrafast response of NPs due to the random NP orientation in solution. Direct inspection of Figure 2a reveals a prominent coherent modulation at the $a$-axis exciton band in the first few picoseconds. In the following, we focus on this feature, which indicates the presence of one (or more) collective mode(s) within the photoexcited NPs. To this end, we first investigate the time evolution of the exciton line shape during the modulation. Figure 2b shows normalized $\Delta A$ spectra at representative time delays during the modulation. The $a$-axis exciton spectral feature is found to undergo a change of asymmetry over time, while maintaining the same peak energy.

Complementary information on the dynamics is obtained by analyzing the time evolution of the signal at different photon energies on the red wing (3.77 eV), the center (3.90 eV) and the blue wing (4.05 eV) of the $a$-axis exciton peak (Figure 3a). In all kinetic traces, the bleach signal rises within the temporal resolution, and then decays exponentially on a time scale longer than our temporal window.$^{32,33}$ Moreover, a giant low-frequency modulation clearly emerges on top and is dramatically damped after one period (with the same frequency) at all probe photon energies. More importantly, all temporal traces across the exciton peak show oscillations in phase, an aspect that is at odds with the behavior expected for an exciton coupled to a coherent collective mode.$^{13,27,34,35}$

To disentangle the different time scales and spectral features that build up the response, we perform a global fit (GF) analysis of the $\Delta A$ signal. We simultaneously fit 13 temporal traces in the 3.60–4.15 eV range of the map in Figure 2a, by fixing the same time constants. Only the use of four exponential functions and two damped sinusoidal terms leads to an excellent fit up to 1 ns. The functions are also convoluted with a Gaussian response that accounts for the pump temporal profile.

Figure 3a shows the results of the GF (solid lines) on top of our data (dotted lines). Importantly, the dynamics can be reproduced only with the use of two damped sinusoidal terms instead of one. Indeed, the first damped sinusoidal function is associated with the large-amplitude oscillation that modulates the negative $\Delta A$ signal in the first ps of the recovery, whereas the second one represents an additional small-amplitude oscillation that appears in the residuals when only the large sinusoidal function is included in the fit. We impose the frequencies of the two sinusoidal terms to be equal at all photon energies, since no significant variations are observed phenomenologically (Figure 3a). The resulting frequencies are $\nu_1 = 290$ GHz and $\nu_2 = 620$ GHz. The GF analysis allows us to separate the spectral components of the two coherent excitations (Figure 3b). Both of them show the largest amplitude around 3.95 eV. Hence, the effect of these modes is to produce a stronger amplitude change of the optical spectrum close to 3.95 eV (i.e., at slightly higher energies than the exciton peak). The oscillation damping time (2.28 ps) is constant at all probe photon energies, indicating that the lifetime is not governed by the optical properties (as the skin depth is much larger than the NP radius) but more by the intrinsic phonon damping. More importantly, within our accuracy, the phases of oscillations do not depend on the photon energy (Figure 3c). This aspect is of pivotal importance, as it sheds light on the detection mechanism of the oscillations in the vicinity of the exciton peak, as further described later.

The frequencies of the oscillatory components are very low compared to those of the optical phonons in anatase TiO$_2$.$^{36}$ Here we demonstrate that they are indeed signatures of coherent acoustic phonons. In bulk single crystals, the frequency of coherent acoustic phonons varies with the probe photon energy.$^{27,36}$ In contrast, in nanosized objects (such as thin films or nanostructures), the confinement of the coherent wavepackets inside the structure leads the mode frequency to be governed by the boundary conditions. In our experiments, the frequency of the coherent oscillations is the
same at different probe photon energies, which suggests a confined nature for the acoustic modes inside the NPs, consistent with the usual assignment. To verify this scenario, we use Lamb’s theory to calculate the eigenfrequencies of the modes supported by a spherical anatase TiO2 NP. In this approach, the NP is treated as a homogeneous elastic sphere embedded in an infinite elastic medium. The anisotropy of the elastic constants and the effects of the surrounding environment are instead neglected. This theoretical treatment is justified for the relatively large NPs investigated here. Through Lamb’s theory, we can assign the two coherent acoustic phonons to the fundamental spheroidal radial mode and its first overtone (i.e., the two first harmonics), with excellent agreement between the computed and experimental values (see Supporting Information). The fundamental mode is also known as “radial breathing mode”, as it causes volume change in the NP and leads to its contraction/expansion.

In order to gain further insight into the mechanism of coherent acoustic phonon generation and detection, we also explored the effect of the excitation density at 4.05 eV (Figure 4a). We observe that the amplitude of the modulation at 3.88 eV scales linearly with increasing fluence (Figure 4b). Depending on the probe photon energy, the modulation depth induced by the coherent acoustic phonons is 4−30% of the total ΔA at all fluences, which is comparable to the changes observed in metallic NPs when the detection is optimized close to the plasmon resonance. The oscillation damping is independent of the excitation density, indicating that the process behind the dissipation of the acoustic energy solely depends on the particle size distribution and the surrounding environment. We also track the time evolution of the exciton peak energy at the different fluences (Figure 4c), finding no sizable shift of the resonance within our experimental accuracy. Also the frequency and the phase of the breathing mode do not vary with fluence, confirming the absence of strong nonlinear effects or the influence of the carrier cooling dynamics on the coherent phonon signal. Hence, these results demonstrate a surprising robustness of the exciton to the coherent strain pulse within the explored fluence range, confirming the validity of the same detection mechanism for all fluences and highlighting its linear response.

We finally address the microscopic origin of the generation and detection mechanisms for the observed coherent acoustic phonons. While the generation mechanism sheds light on the interaction between the photoinduced uncorrelated carrier density and the acoustic field, the detection process reveals how the coherent acoustic phonons influence the excitonic resonances. Importantly, these two processes involve distinct bands and electron–hole distributions and, as such, may be governed by very different microscopic mechanisms.

The generation mechanism of coherent acoustic phonons in nonmagnetic and nonpiezoelectric materials is based on the competition between the nonthermal deformation potential (DP) coupling (electronic pressure) and the thermoelastic (TE) coupling (phononic pressure). In order to establish the main process involved in the generation mechanism, one needs to calculate the relative strengths of the two components to the photoinduced stress (σDP/σTE). If σDP/σTE ≪ 1, the TE coupling governs the coherent strain. In simple band insulators and semiconductors, the strength of the DP is typically higher. In the case of anatase TiO2, the coupling between the carriers and polar optical phonons is so strong that the photoexcited carriers relax to the bottom of the respective bands in ∼50 fs. This indicates that the TE coupling can compete with the DP for the coherent acoustic phonon excitation process. To estimate the DP contribution to the photoinduced stress (σDP), we rely on the following expression

![Figure 4](https://example.com/figure4.png)

**Figure 4.** (a) Time evolution of ΔA at 3.88 eV for different values of absorbed pump fluence. (b) Fluence dependence of the coherent acoustic phonon amplitude. (c) ΔA spectra at the maximum coherent acoustic phonon response as a function of absorbed pump fluence. (d) Pump photon energy dependence of the coherent acoustic phonon signal. The three curves have been vertically shifted for clarity.
\[
\sigma_{\text{DP}} = \sum_k \delta n(k) \frac{dE_k}{dn}
\]

where \( \delta n(k) \) is the change of the electronic density at level \( k \) and \( dE_k/dn \) is the DP parameter. As the photocarriers thermalize to the respective band edges at \( \Gamma \) and \( \sim X \) within 50 fs, we simplify eq 1 as

\[
\sigma_{\text{DP}} = -nB \left[ \frac{dE}{d\sigma} + \frac{dE}{d\sigma} \right] = -nB(d_\parallel + d_\perp)
\]

where \( n \) is the photoinduced carrier concentration and \( B \) is the bulk modulus.

The phononic contribution to the photoinduced stress \( \sigma_{\text{TE}} \) can be written as

\[
\sigma_{\text{TE}} = -\alpha_i B \Delta T_L = -\alpha_i n E_{\text{exc}} / C_L
\]

where \( \alpha_i \) is the volumetric thermal expansion coefficient. For a tetragonal crystal, \( \alpha_i = 2 \alpha_\parallel + \alpha_\perp \), where \( \alpha_\parallel \) and \( \alpha_\perp \) are the in-plane and the out-of-plane thermal expansion coefficients, respectively. \( \Delta T_L \) is the change in lattice temperature, \( C_L \) is the lattice heat capacity per unit volume and \( E_{\text{exc}} \) is the excess energy as measured relative to the optical bandgap energy. The quantity \( \sigma_{\text{DP}} / \sigma_{\text{TE}} \) reads

\[
\frac{\sigma_{\text{DP}}}{\sigma_{\text{TE}}} = \frac{C_L (d_\parallel + d_\perp)}{\alpha_i E_{\text{exc}}}
\]

To evaluate this expression, we use \textit{ab initio} methods and calculate \( d_\parallel \) and \( d_\perp \). Specifically, we compute the single-particle electronic structure of anatase TiO\(_2\) at the GW level of theory for varying strengths of the unit cell isotropic deformation (see Supporting Information). This hydrostatic pressure mimics the use of a broadband probe in ultrafast optical spectroscopy and the intensity of the coherent oscillation shows a quadratic dependence on the derivative of the absorption spectrum.\(^\text{13,45}\) This is the typical condition observed for most phonon–exciton coupling phenomena in the time-domain.\(^\text{36}\) In contrast, in the less conventional \textit{amplitude modulation} scenario, it is the intensity of the peak in the absorption spectrum that varies with time while the resonance energy is fixed. As a result, the coherent phonon phase remains constant over the resonance. The microscopic origin behind these effects is related to the particular parameter of the electronic Hamiltonian that is modulated by the ionic motion. In the case of an energy modulation, the band structure is modulated by the coherent phonon via the DP mechanism. As a consequence, an energy renormalization occurs for both the excitonic and the interband charge excitations. In the much less frequent amplitude modulation, the ionic motion acts directly on other parameters of the electronic Hamiltonian, such as (i) the site-to-site hopping integral of an electron, modifying the electronic bandwidth and thus the density of states, and/or (ii) the transition dipole moment associated with an interband transition, thus creating a Herzberg–Teller wavepacket.\(^\text{47,48}\)

The modification of the electronic density of states appears as a more likely explanation in the case of anatase TiO\(_2\). Indeed, excitons are of the charge-transfer type in this material, being formed by holes in oxygen 2p states and electrons in titanium 3d states. During the expansion and contraction of the NPs induced by the acoustic breathing mode, the Ti–O distances are periodically modified, leading to a modulation of the overlap between the relevant orbitals contributing to the many-body exciton state. As a result, the hopping integral between the two lattice sites and the electronic density of states are readily affected. To our knowledge, this effect has never been directly observed and selectively controlled.

To conclude, our experimental data clearly show the amplitude modulation of an excitonic resonance in anatase TiO\(_2\) during the coherent ionic motion. The modulation is caused by the breathing mode of the NP and its first overtone, which are shown by many-body perturbation theory to be generated from the deformation potential coupling. At this stage we cannot conclude whether the pronounced amplitude modulation is due to a change in the density of states, a change in the transition dipole moment of the excitonic transition or both, but the overall result is remarkable and unique. It also offers the possibility of applications in the field of sensors, especially considering that anatase TiO\(_2\) is a cheap material and is already embedded in a large range of devices. In this respect, future efforts to increase the coherence time of the confined wavepackets, e.g., by using monodisperse ensembles of NPs and embedding them in an acoustic impedance-mismatched matrix, will allow to achieve long-lasting modulations of the exciton oscillator strength.

**Methods. Nanoparticle Synthesis and Characterization.** The TiO\(_2\) NPs were prepared using the sol–gel method.\(^\text{28}\) The details of the synthesis procedure are provided in the Supporting Information. Sample characterization by means of X-ray diffraction and transmission electron microscopy is provided is refs.\(^\text{39,50}\) Such characterization demonstrate the good quality of the anatase phase and the spherical shape (with an average diameter of approximately 25 nm) of the NPs. Furthermore, the room temperature steady-state absorption spectrum of the anatase TiO\(_2\) NPs was measured and shown in ref 19.

**Ultrafast Broadband Deep-UV Spectroscopy.** The ultrafast broadband deep-UV spectroscopy measurements have been performed using a setup described in detail in ref 29. The narrow-band deep-UV pump and the broadband deep-UV
probe are focused and overlapped in time and space onto the sample with the same polarization. To ensure that the probed region is homogeneously illuminated, the typical spot size of the pump and the probe are 100 × 150 μm² and 40 × 44 μm² full-width half-maximum, respectively.

Photodamage of the sample was prevented by circulating the colloidal solution into a 0.2 mm thick quartz flow-cell. The concentration was approximately 0.4 at the pump photon energy of 4.05 eV. The probe was transmitted through the sample and then detected at a repetition rate synchronized with the laser. A motorized delay line was used to vary the time delay of the probe with respect to the pump beam, and measure the difference between the probe absorption with and without pump pulse for each time delay. A multimode optical fiber (100 μm) is used to collect the transmitted broadband probe and then coupled to the entrance slit of a 0.25 m imaging spectograph (Chromex 250i). The beam was dispersed by a 150 gr/mm holographic grating and imaged onto a multi-channel detector consisting of a 512 pixel CMOS linear sensor (Hamamatsu S11105, 12.5 × 250 μm pixel size) with up to 50 MHz pixel readout. Shot-to-shot detection was easily achieved as the maximum read-out rate per spectrum was almost 100 MHz pixel readout. Shot-to-shot detection was easily achieved, at the expenses of a reduction of the probe bandwidth in the achromatic frequency doubling scheme.

**Many-Body Perturbation Theory Calculations.** Many-body perturbation theory at the GW level was used to calculate the electronic structure of bulk anatase TiO₂. Specifically, we utilized the BerkeleyGW package on-top of eigenvalues and eigenfunctions obtained from density-functional theory (DFT). We used the plane-wave pseudopotential implementation of DFT as provided by the package Quantum Espresso. The DFT calculations were performed using the generalized gradient approximation (GGA) as in the Perdew–Burke–Ernzerhof (PBE) scheme for the exchange-correlation functional. The Ti norm-conserving pseudopotential was generated in the Rappe–Rabe–Kaxiras–Joannopoulos (RRKJ) scheme, including semicore 3s and 3p states. While standard structural and electronic quantities are already converged in DFT with an energy cutoff of 90 Ry, the energy cutoff used here was raised to 160 Ry to properly include the high number of bands necessary to reach convergence for the many-body evaluated properties. Bulk anatase TiO₂ was modeled on a body-centered tetragonal lattice containing 2 Ti and 4 O atoms (primitive cell) with lattice parameters (optimized at the PBE level) α = b = 3.79 Å and c = 9.66 Å. The ground state electronic density is properly described with a coarse 4 × 4 × 4 k-point grid for sampling of the BZ. The GW quasiparticle corrections to the DFT eigenvalues were performed at the one-shot level of theory (GₐWₒ). We computed the polarizability and inverse dielectric matrices in BerkeleyGW by employing a total of 2474 CBs and G-vectors with kinetic energies up to 46 Ry, whereas the self-energy operator was computed using 2472 unoccupied bands and a G-vector cutoff energy of 46 and 160 Ry for the screened and bare Coulomb matrices, respectively. The electronic band structures were obtained by interpolating the GW corrections in the 4 × 4 × 4 grid into PBE energies calculated for the k-points along the symmetry lines Z–Γ and Γ–X.

To estimate the role of the electron-acoustic phonon coupling in the electronic properties of anatase TiO₂, we performed frozen phonon DFT + GW calculations by applying a hydrostatic (both compressive and tensile) strain of 0.1% and 1%. The results are shown in the Supporting Information.

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