p-State Luminescence in CdSe Nanoplatelets:
The Role of Lateral Confinement and an LO-Phonon Bottleneck

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We report excited state emission from p-states at excitation fluences well below ground state saturation in CdSe nanoplatelets. Size dependent exciton ground state-excited state energies and dynamics are determined by three independent methods, time-resolved photoluminescence (PL), time-integrated PL and Hartree renormalized \( k \cdot p \) calculations—all in very good agreement. The ground state-excited state energy spacing strongly increases with the lateral platelet quantization. Our results suggest that the PL decay of CdSe platelets is governed by an LO-phonon bottleneck, related to the reported low exciton phonon coupling in CdSe platelets and only observable due to the very large oscillator strength and energy spacing of both states.

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Semiconductor nanoparticles have attracted growing attention in the last decade due to their promising optical and electronic properties. Two dimensional II-VI semiconductor nanoplatelets (NPLs) gained increasing interest due to their unique electronic and optical properties [1], such as the Giant Oscillator Strength effect [2–4], room temperature exciton coherence [3] and lasing [5], strong electroabsorption response [3] and size dependent dark-bright splitting [2]. With this letter we report on energies and dynamics of excited state emission from p-states in CdSe nanoplatelets by the means of temperature and time-resolved photoluminescence (PL) and Hartree renormalized \( k \cdot p \) modeling. Figure 1 shows the evolution of the lowest exciton s and p-states with increasing transversal confinement and anisotropy in CdSe NPLs.

We show in this letter that the ground state-excited state energy difference of CdSe NPLs strongly increases with the lateral platelet quantization and that the already described bi-exponential PL decay of NPLs is connected to the very large dipole moments of the excited state (ES) and ground state (GS) and a phonon bottleneck suppressing inter-relaxation. A dynamic thermal equilibrium between both states mediated by LO phonon scattering is observed. The strong transversal confinement related suppression of LO phonon modes in the NPLs [3], also observed as lifetime limited dephasing rates [4], results here in a slowdown of the ES–GS exciton transfer rate and subsequent visible ES luminescence well below ground state saturation. We show that the high energy emission originates systematically from the NPL’s ES and correlates to the lateral confinement dependent ES–GS energy difference. Colloidal 4.5 monolayer (ML) CdSe NPLs were synthesized, characterized by TEM and embedded in PMAO films on thin fused silica substrates mounted in a liquid He cryostat according to detailed description in the Supporting Material. Our experimental setup allows the consecutive measurement of time-integrated (CCD-spectrometer) and time-resolved (streak camera) fluorescence of a sample with confocal excitation in the platelet absorption continuum (420 nm, SHG of a 75.4 MHz/150 fs Ti:Sa laser) and detection through an (NA=0.4) objective. The excitation density was held below moderate 0.2 W/cm\(^2\) to avoid any heating, saturation and the presence of biexcitons (we estimate only < 0.1 percent of the platelets are excited within one laser pulse using ICP and absorption cross sections of She et al. [2]).

The PL spectra of the investigated CdSe core NPLs are displayed in Fig. 2 (a) showing a dual emission. Voigt-
fits are used to determine the peak centers of the ground and excited state emission plotted vs. temperature as open (GS) and solid (ES) red dots vs. temperature. (b) Phonon Bottleneck: ES–GS integrated PL intensity ratios deduced from (a) vs. the ES–GS energy spacing at 4 K and 22 K. (c) Transient PL decay and evolution of the ES and GS emission with time and exemplary Voigt fits (platelet size 29x8 nm²).

To assess the luminescence dynamics of both PL emissions we apply time-resolved PL using a streak camera in two different time scales. Fig. 2 (c) displays a PL transient of 29x8 nm² platelets along with spectral cuts in time showing the evolution of the dual ES–GS emission. A fast ES PL decay and a slower GS PL decay can be observed and separated by fitting the spectral contributions vs. time (Figure 3 (a) lower part).

FIG. 3. Blue lines: Representative examples of photoluminescence decay curves at 4, 35 and 100 K of CdSe NPLs with lateral size of 29x8 nm² (panels a and b) and 41x13 nm² (panels c and d). The bi-exponential fits (on top of data) to the fast time-range decays (a and c) use the long decay time derived from mono-exponential fits to the curves in (b) and (d) recorded in a wider time window. The instrument response function (green line) is used for deconvolution. (a) lower panel: ES (red) and GS (black) transients obtained from Voigt fits in Fig. 2 (c). Inset: Spectrally dispersed Streak Camera image of the PL decay in the first 0.5 ns of 29x8 nm² CdSe NPLs at 4 K. Excited state emission is clearly visible. The time range of panel (a) is indicated by a grey frame.
The observed increase of the ES–GS energy spacing with confinement (Fig. 4(a)) is expected for a strongly confined system. Further, e.g. for the 29x8 nm² NPLs the low temperature scattering rate \( \gamma_0 \) (\( \gamma_0^{-1} = 8 \cdot 10^{10} \text{s}^{-1} \) for \( T \to 0 \text{ K} \)) of the rate equation model, representing the phonon bottleneck, is in good agreement with the fast rise kinetics of the ES–GS emission (12 \( \cdot 10^{10} \text{s}^{-1} \)) derived from Fig. 3(a). This is an additional confirmation of the existence of a phonon bottleneck dominating the ES–GS dynamics in CdSe NPLs. The strong transversal confinement related suppression of energetically matching LO phonon modes in the NPLs [3], also observed as lifetime limited dephasing rates [4], results here in a slowdown of the ES–GS exciton transfer rate. For our platelets of different lateral size this LO phonon bottleneck is also observed in the ratios of the time integrated ES–GS emissions when correlated to the corresponding ES–GS energy spacings in Figure 2(b). A clear minimum can be seen as the spacing approaches the CdSe platelet LO phonon energy of 25.4 meV [16] (plotted for exemplary temperatures of 4 and 22 K). In case of resonance the high density of LO phonons energetically matching the ES–GS spacing leads to a fast relaxation of the ES population to the GS resulting in a small ES–GS intensity ratio. In the off resonant cases for low and high ES-GS spacings the ES→GS relaxation is more suppressed leading to a higher ES contribution to the emission. This is again a clear manifestation of a phonon bottleneck in our NPLs. In the following we will compare our experimental ES-GS energy differences with theoretical calculations.

The samples considered in this work, have different lateral sizes in \( l_x \) and \( l_y \) direction and a much smaller thickness \( l_z \). For such structures, excited states (p-states), energetically well separated from the ground state, are expected. Figure 1 shows the evolution of the electron p-shell as the level of structural anisotropy increases up to \( l_x > l_y > l_z \). In this case the \( p_x \) state constitutes the lowest excited state followed by the \( p_y \) and the \( p_z \) state. As the vertical platelet dimension is very small, the \( p_z \) state is expected at very high energies. A similar reasoning applies to the excited hole states. Fig. [5] provides an overview of the lowest allowed optical transitions: The ground state transition occurs between the electron and hole s-states, the first excited state transition is related...
to the lowest $p$-states, which we label $p_x$, as the $x$-axis corresponds to the longest axis of the platelet.

The electronic properties and optical transitions of our 4.5 ML CdSe NPLs are calculated in accordance with TEM data (Supporting Material). Following our previous work\cite{1} the electronic structure is obtained using a 3D implementation of eight-band $k \cdot p$ envelope function theory. The Coulomb interaction is taken into account via a Hartree self-consistency cycle, performed separately for electron and hole ground state and their first excited states. Both, the effects arising from the dielectric environment and the electron and hole self-energy are included. The calculated heavy hole transition energies are compared to experimental values in Table 1 (Supplementary Material): $E_{GS}$ corresponds to the calculated energy of the ground state exciton, and $\Delta E^{(\text{Theo})}$ is the energy difference to the excited state transition, $\Delta E = E_{GS} - E_{ES}$ shown in Figure 4 (a). The theoretical and experimental values of both quantities show a very good agreement (see also supp. Material), thus, supporting the direct observation of an excited state - ground state energy spacing $\Delta E$ in our experiments.

In summary we have shown that CdSe NPLs exhibit not only lowest hh s-exciton state (GS) related photoluminescence upon continuum excitation, but also p-state (ES) luminescence far below GS saturation. Calculations and time integrated PL show a strong increase of the ES–GS energy spacing from about 18 to 36 meV with increasing quantization of the exciton wavefunction. The existence of a phonon bottleneck between ES and GS is confirmed by three methods: A rate equation model for the temperature dependence, the temporal course of ES and GS emission and the observation of an ES/GS intensity ratio minimum in the time-integrated PL for size dependent ES–GS energy spacings resonant to the LO phonon energy of 25.4 meV in the CdSe NPLs. We conclude further that the presented double emission in PL is not related to an LO phonon replica, which would have the same GS dynamics and a practically confinement independent energy spacing to the GS emission. In contrast the observed bi-exponential PL decay of nanoplatelets is related to a phonon bottleneck between ES and GS populations.

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