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Probing Excitons in Ultrathin PbS Nanoplatelets with Enhanced Near-Infrared Emission

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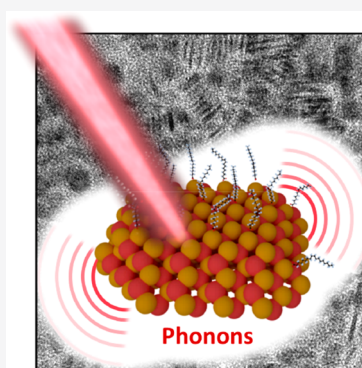


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Supporting Information

ABSTRACT: Colloidal PbS nanoplatelets (NPLs) are highly interesting materials for near-infrared optoelectronic applications. We use ultrafast transient optical absorption spectroscopy to study the characteristics and dynamics of photoexcited excitons in ultrathin PbS NPLs with a cubic crystal structure. NPLs are synthesized at near room temperature from lead oleate and thiourea precursors; they show an optical absorption onset at 680 nm (1.8 eV) and photoluminescence at 720 nm (1.7 eV). By postsynthetically treating PbS NPLs with CdCl₂, their photoluminescence quantum yield is strongly enhanced from 1.4% to 19.4%. The surface treatment leads to an increased lead to sulfur ratio in the structures and associated reduced nonradiative recombination. Additionally, exciton–phonon interactions in pristine and CdCl₂ treated NPLs at frequencies of 1.96 and 2.04 THz are apparent from coherent oscillations in the transient absorption spectra. This study is an important step forward in unraveling and controlling the optical properties of IV–VI semiconductor NPLs.



Ultrathin 2D colloidal semiconductor nanosheets (NSs) and nanoplatelets (NPLs) are highly topical materials with interesting optoelectronic properties strongly different from their spherical nanocrystal (NC) or solid-state counterparts. In contrast to II–VI semiconductor NPLs (e.g., CdSe) exhibiting strong absorption and photoluminescence (PL) in the visible range,^{1–3} IV–VI semiconductors are of interest due to their widely tunable band gap and photoluminescence from the far-infrared to the near-infrared (NIR) by variation of the thickness of the NSs.^{4,5} Covering the NIR range is crucial for advancing the spectral window inaccessible by CdSe-based NPLs without additional treatment including doping^{6,7} or shell-growth.^{6,8} In addition, exciton binding energies and charge carrier mobilities in 2D PbS can also be tuned by the thickness of the NSs. For example, thin PbS NSs exhibit stable excitons with high binding energies (~70 meV for 4 nm thickness) and carrier multiplication (CM) efficiencies approaching 100%, meaning that all photons with an energy exceeding the CM threshold generate additional electron–hole pairs.^{9–11} Charge carrier mobilities increase with the thickness of the PbS NSs and become as high as 1000 cm²/(V s) for 16 nm thick NSs, which is close to the bulk mobility of PbS, while absorbing more light at longer wavelengths than thin NSs. Typically, PbS NSs with lateral dimensions of several micrometers and a thickness in the range of 4–40 nm are obtained by synthesis methods based on oriented attachment.^{12–14} Recently, new colloidal synthesis methods for further decreasing the thickness of 2D PbS layers down to atomically thin PbS NPLs have been implemented, including a combination of surface ligand stabilization¹⁵ as well as

kinetically controlled reaction conditions.^{16,17} These methods yield ultrathin 2D PbS layers with controllable lateral size as reaction product.^{15,18,19} For example, ultrathin (1–2 nm) PbS NPLs were synthesized using the single-source precursor lead thiocyanate, and yielded NPLs with an orthorhombic crystal structure and high photoconductivity,¹⁹ while the absorption of PbS NPLs synthesized from lead octadecylxanthate was optically tuned, albeit showing weak NIR PL.²⁰

In this work, we elucidate the characteristics and dynamics of photoexcited electronic states (excitons) in ultrathin PbS NPLs by using ultrafast transient optical absorption spectroscopy. We study cubic rock-salt phase PbS NPLs obtained by a near room temperature synthesis method using lead oleate and thiourea precursors (see Scheme 1, Figure 1, and Figure S1 and the experimental part in the Supporting Information). Synthesis conditions are chosen following Hendricks et al.²¹ such that pure lead oleate is used, instead of producing it *in situ* from oleic acid and lead acetate.^{15,22} The procedure of presynthesizing lead oleate for the reaction is necessary to obtain the best results in terms of PbS NPL shape, size, and optical properties (see Figure 1, Figures S1 and S6). The reaction is carried out in octylamine with oleic acid and thiourea as the sulfur precursor. Exploiting an acid–base

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Scheme 1. Schematic of PbS NPLs Stacked on Edge and Lying Flat As Observed in the TEM Images Shown in Figure 1A

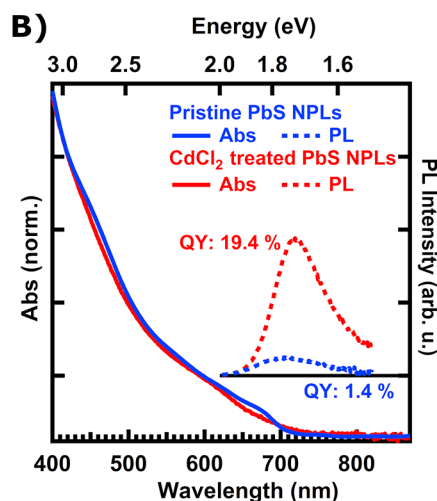
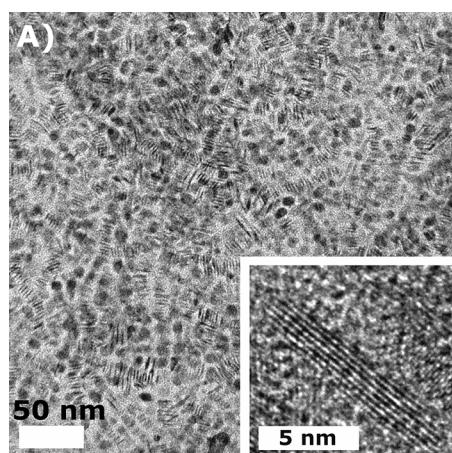
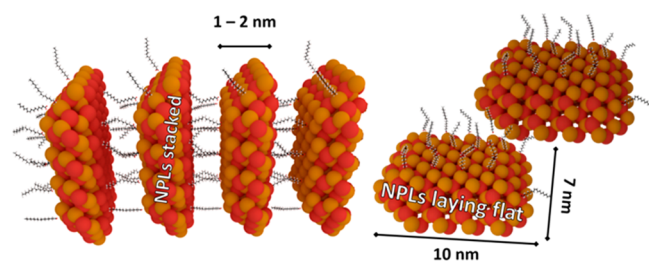


Figure 1. (A) TEM images of ultrathin PbS NPLs with lateral dimensions of $7 \times 10 \text{ nm}^2$ and a thickness of 1–2 nm. Some NPLs are stacking on edge as shown in Scheme 1. The inset shows a single NPL on its edge. (B) Steady-state absorption and PL spectra of pristine PbS NPLs (blue) and after treatment with CdCl_2 (red), showing the absorption onset of the pristine NPLs at 680 nm (1.8 eV) and PL centered at 720 nm (1.7 eV) and broad absorption of the CdCl_2 treated sample with a slight rise near 620 nm (2.0 eV). The photoluminescence quantum yield of CdCl_2 treated PbS NPLs reaches 19.4%.

equilibrium between octylamine and oleic acid, which leads to the formation of an ammonium (RNH_3^+) species that supports the growth of 2D NPLs,²³ we obtain slightly elongated 2D PbS NPLs with a width of 7 nm and a length of 10 nm (see Figure 1A, Figure S1, and Scheme 1). The NPLs exhibit an absorption

edge at 680 nm (1.8 eV) and NIR PL at 720 nm (1.7 eV) with a QY of 1.4% (see Figure 1B).

The obtained NPLs show the typical reflexes of the cubic PbS crystal system (see Figures S2 and S3 for powder XRD and SAED transmission electron microscopy rotational scans of the samples). EDS analysis yields a stoichiometric ratio of 1.1:1 for Pb:S in pristine NPL samples. In a postsynthetic step, the photoluminescence quantum yield (PLQY) of pristine PbS NPLs is increased to 19.4% by treating the crude reaction product with a CdCl_2 solution in octylamine (see the Supporting Information). Recently, Christodoulou et al. reported an increase in the thickness of CdSe NPLs after treating the samples with CdCl_2 with which the authors obtained CdSe NPLs with a thickness inaccessible under typical reaction conditions.³ Generally, the surface treatment of NCs with metal halides leads to their stabilization and increase of their size.^{24–28} In our case, after treating the pristine NPLs with CdCl_2 , we find PbS layers with a slight regularity loss (see Figure S4) and an increased Pb:S ratio of 1.8:1 following EDS analysis, which resembles a lead rich surface typically found for PbS NCs.²⁹ A higher Pb:S ratio in CdCl_2 treated samples suggests the addition of Pb to the surface and/or edges of the NPLs, which is a reconstruction effect, as reported for CdSe NPLs³⁰ and NCs.³¹ The lack of a significant absorption shift to shorter wavelengths (see Figure 1) and a Cd:Cl atomic ratio of 1:2 in CdCl_2 treated samples (see Figure S5 and Table S1) further excludes the growth of a CdS shell on the PbS NPLs or cation exchange which is, e.g., observed in PbS NC samples.³² Figure 2 shows the Jacobian wavelength to energy converted

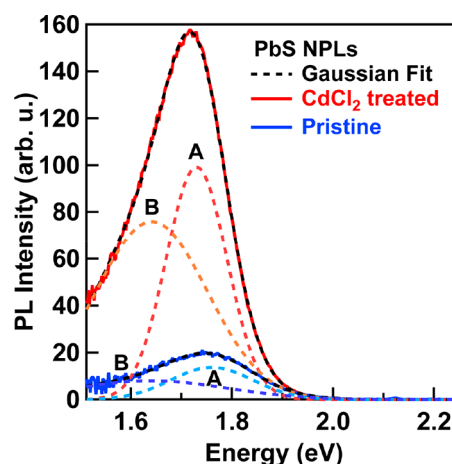


Figure 2. PL spectra of pristine (blue trace) and CdCl_2 treated (red trace) PbS NPLs. The emission is fit with a sum of two Gaussians (black dashed traces) with the two corresponding components A and B shown in lighter dashed lines.

steady-state PL spectra of pristine and CdCl_2 treated PbS NPLs in more detail.³³ Generally, PbS NCs exhibit a rather broad PL at room temperature, which was attributed to two emissive states in the NCs by Caram et al.³⁴ The authors ascribe PL from the PbS NC band edge as well as PL from an emissive “pinned” trap state in NCs to be responsible for PL line width broadening. Indeed, we find PbS NPL PL spectra are best fitted with the sum of two Gaussians (see Figure 2 and the fit function in the Supporting Information) for pristine and CdCl_2 treated samples.

Prior to the CdCl_2 treatment, PbS NPLs exhibit a band gap associated PL peak labeled A at 1.76 eV (705 nm) with a fwhm

of 192 meV (see Table 1 and Figure 2). After the treatment, the PL peak A at 1.73 eV (717 nm) shows a decreased fwhm of

Table 1. Values for the Two Gaussian Fits of the PbS NPL PL

PbS NPLs	peak center (eV)		fwhm (meV)		peak area		peak ratio A:B
	A	B	peak A	peak B	A	B	
pristine	1.76	1.64	192	356	2.80	3.03	0.93
CdCl ₂ treated	1.73	1.64	142	260	15.0	21.0	0.72

142 meV. The “pinned” trap state associated peak labeled B stays fixed prior to and after the CdCl₂ treatment at 1.64 eV (756 nm). Both PL contributions A and B are strongly enhanced (albeit with an increasing contribution of B) after the CdCl₂ treatment, rendering it effective in increasing the overall PLQY of PbS NPLs.

As shown in Figure 1, CdCl₂ treated PbS NPLs exhibit a smaller absorption strength at 680 nm (1.8 eV) than pristine PbS NPLs and a slight rise in absorption near 620 nm (2.0 eV).

To further characterize the nature and dynamics of photoexcited states in pristine and CdCl₂ treated PbS NPLs, we apply ultrafast transient optical absorption (TA) spectroscopy as described in refs.^{35–38} and briefly in the Supporting Information. The samples are photoexcited close to the band edge at 700 nm (with an optical density of ≤ 0.1) to prevent dynamic effects by charge carrier cooling and with the same photoexcitation density (2.5×10^{13} photons/cm²) so that the distribution of the number of excitons in both NPL samples is similar.

The shape of the TA spectra in Figure 3 is discussed below on the basis of the terminology of electronic transitions and exciton states obtained from TA studies on PbSe^{37,39} and PbS NCs.^{36,40} Figure 3A,C shows 2D color-coded contour TA spectra of pristine and CdCl₂ treated PbS NPLs for comparison. The TA spectrum of pristine PbS NPLs exhibits a prominent negative ground-state (gs) bleach feature (1) of the $1S_h-1S_e$ transition at 673 nm due to state filling and stimulated emission, also observed in the spectral line cuts in Figure 3B. The maximum of gs bleach 1 is slightly blue-shifted with respect to the steady-state absorption at 680 nm (see Figure 1) implying a red shift in the excited-state absorption due to the formation of biexcitons by the probe pulse.³⁹ The small bleach feature (2) originates from the formally forbidden $1S_h-1P_e/1P_h-1S_e$ transitions that become slightly allowed in NCs due to symmetry breaking.^{39,41} At shorter wavelengths, we probe the derivative-like feature (3) that we attribute to a red-shifted ground-state absorption due to biexciton interactions.^{42–44} We probe a wavelength-independent broad induced absorption at sub-band gap energies persisting over the TA time range studied (2.7 ns). This can be due to photoexcitation of trapped charges and/or due to further excitation of an exciton by the probe pulse, leading to intraband transitions.^{45,46} The TA spectra of CdCl₂ treated PbS NPLs are very different from those of the pristine NPLs. Strikingly, they show two bleach features ((1a) and (2a)) at 677 and 613 nm with similar amplitudes and a long lifetime exceeding 3 ns (see Figure 3C,D). Since both bleach features are present for

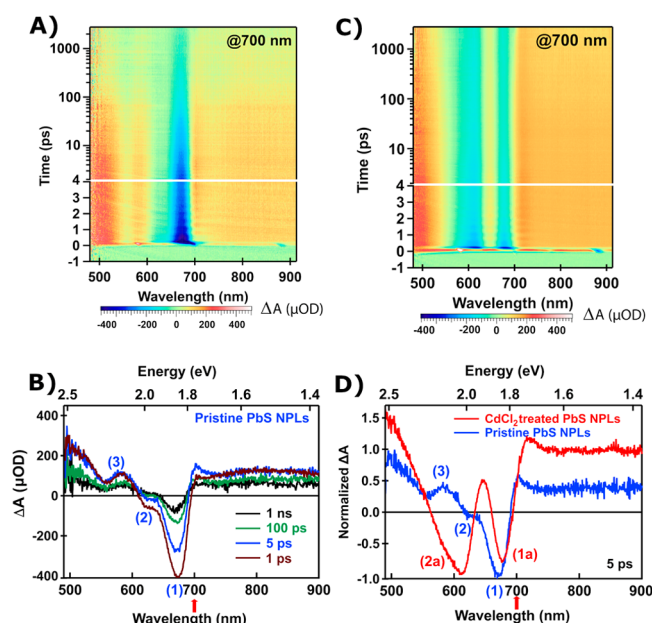


Figure 3. Color-coded 2D TA spectra of PbS NPLs photoexcited at 700 nm. (A) Pristine PbS NPLs exhibit one prominent bleach feature (1) at 673 nm. Additional features (2) and (3) and spectral line cuts at different times after photoexcitation are plotted in (B) and discussed in the text. (C) CdCl₂ treated NPLs show a strong effect of the treatment. (D) includes spectral line cuts taken from (A) and (C) at a delay time of 5 ps after photoexcitation, with CdCl₂ treated samples showing two prominent bleach features at 677 nm (1a) and 613 nm (2a). TA spectra are very distinct due to the involvement of different electronic states in the two samples as discussed in the text.

photoexcitation at a substantially longer wavelength (700 nm) than bleach feature (2a) at 613 nm, we exclude the latter being caused due to band edge excitons of thinner PbS NPLs after the CdCl₂ treatment. The strong bleach feature (2a) must be due to an additional electronic state introduced by the CdCl₂ treatment. In addition, the CdCl₂ treated PbS NPLs exhibit an increased induced absorption between features (1a) and (2a) and a stronger sub-band gap trap state and intraband absorption.⁴⁵

Figure 4 includes the decay dynamics of the TA signal probed at the highest amplitude of the different bleach features for pristine and CdCl₂ treated PbS NPLs observed in Figure 3. The normalized decays show that bleach features (1a) and (2a) level off at approximately 20% of the original signal intensity after 20 ps, while bleach feature (1) decays over the time range of the measurement (15% of the original signal intensity after 20 ps and 5% after 2.7 ns). The larger bleach at long times in CdCl₂ treated PbS NPLs agrees well with the higher QY found in the samples.

Interestingly, we probe coherent oscillations in the TA spectra of PbS NPLs at short times after photoexcitation, as shown in the inset of Figure 4. Fourier transformation and a Lorentzian fit to the data of the short-time decay curve residuals yields frequencies of 1.96 THz (8.1 meV, 65.4 cm⁻¹) for pristine and 2.04 THz (8.4 meV, 68.1 cm⁻¹) for CdCl₂ treated NPLs (see Figure S7 and S8). These values correspond well with exciton–phonon coupling in pristine and CdCl₂ treated PbS NPLs to bulk-like optical and/or acoustic phonon modes of PbS at 1.96 THz (8.1 meV, 66 cm⁻¹) and 2.1 THz (8.4 meV, 68 cm⁻¹) respectively.^{47–50}

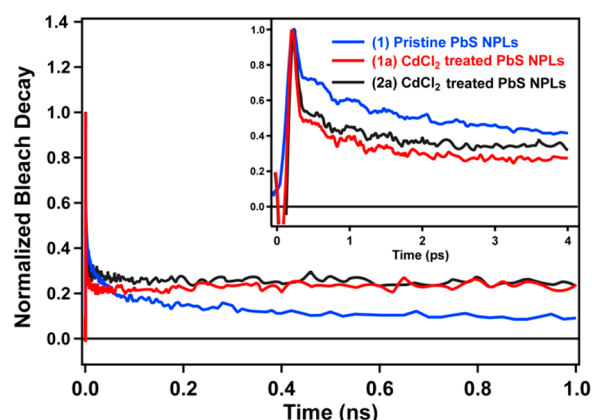


Figure 4. Decay dynamics of bleach features (1) of pristine and (1a) (red) and (2a) (black) of CdCl_2 treated PbS NPLs with transients for pristine NPLs decaying over the course of the measurement and with CdCl_2 treated sample transients leveling off at 20% of the original signal strength. The inset shows coherent oscillations originating from exciton–phonon interactions in PbS NPLs.

In conclusion, we have studied the optical properties of strongly quantum-confined colloidal cubic 2D PbS NPLs synthesized at near room temperature by steady-state PL and ultrafast TA spectroscopy for the first time. A new synthesis as well as a postsynthetic treatment of the obtained PbS NPLs with CdCl_2 increases their lead to sulfur ratio and leads to a strongly enhanced PLQY of 19.4%. Additionally, coherent oscillations probed by TA originate from strong exciton–phonon interactions in PbS NPLs. Our results render the surface treatment as a valuable tool for tuning the optical properties of PbS NPLs for near-infrared emission.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.0c03461>.

Synthesis of PbS NPLs, additional TEM images, XRD, intensity profiles, EDS spectra, elemental analysis, PLQY analysis, and brief description of the TA spectroscopic measurements (PDF)

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Notes

The authors declare no competing financial interest.

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