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Room temperature photobrightening and low temperature photodarkening in two-dimensional CdSe nanoplatelets†

Colloidal nanoplatelets are atomically flat quasi-two-dimensional colloidal particles of semiconductors which have been a topic of intense study for their optical properties and potential applications. Like for the previous generation quantum dots, the photostability of nanoplatelets remains a topic of concern that must be understood to reliably use them in devices. We have found that the photoluminescence intensity from CdSe nanoplatelets on continuous laser excitation displays a significant rise (photobrightening) over time at temperatures above 215 K. Conversely, a darkening effect is found below 215 K and the extent of photodarkening is systematically enhanced with the increase in the excitation power density. The darkening processes can be systematically reversed through sub-room temperature thermal annealing, suggesting an activated recovery process with a gap of about 55 meV. The photobrightening and photodarkening are inferred to be occurring on account of the photodamage and thermally assisted healing of oleic acid, the capping ligand commonly used for passivation and functionality. A significant enhancement of photobrightening is further observed around 250 K, in the vicinity of the phase transition of oleic acid. This work thus highlights the fundamental role of the ligand-surface interaction in controlling the photoluminescence efficiency of nanoplatelets.

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Introduction

Colloidal nanoplatelets (NPLs) are emerging two-dimensional (2D) materials. 1-4 Significant interest in these structures arises from the fact that semiconductor NPLs not only possess properties of colloidal semiconductor quantum dots, which have found wide-spread application in electronics and optoelectronics, 4-10 but also show novel features absent in previous generation nanocrystals. 11,12 Hence, semiconductor NPLs are highly promising materials with potential for the next generation light emitter devices, 2,13-15 lasers, 2,16 photodetectors, and photosensors. 17,18 Additionally, their large surface-to-volume ratio offers opportunities for surface modification and functionalization, enhancing their compatibility with diverse biological and sensing applications. 1 Despite the remarkable properties, the photostability of nanocrystals under laser excitation has been an issue of concern. It has been previously reported for nanocrystals that photoexcitation of the CdSe directly

influences the interaction between the ligand and the core, ¹⁹ thereby affecting the PL quantum yield. Additionally, order–disorder phase transitions²⁰ and ligand-mediated phase transitions²¹ have also been reported for nanocrystals. The photoluminescence (PL) characteristics of NPLs exhibit a significant reliance on the ligand behavior, excitation parameters, and ambient surroundings. For instance, when subjected to continuous excitation, both quantum dots and NPLs display intermittent blinking patterns, ²² photobrightening, ²³ and photodarkening phenomena. ^{24–31} Since these features determine the device performance, they need to be

In this article, we report a low temperature photodarkening T < 215 K and a converse photobrightening near room temperature $T \ge 215$ K in CdSe NPLs, when subjected to continuous laser excitation. The photobrightening is attributed to thermally activated photodamage repair in oleic acid ligands and its drastic enhancement around 250 K also correlates to the phase transitions in oleic acid. Photodarkening, whose rate is dependent on the laser excitation power, is attributed to ligand desorption from the surface caused by continuous laser excitation and insufficient passivation of defects by oleic acid. Furthermore, the ligand repair becomes less effective at low temperatures due to its freezing. Remarkably, the darkened state exhibits stability over 24 hours, when the temperature is kept fixed at 80 K. Photodarkening is

reported for nanocrystals that photoexcitation of the CdSe directly

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nevertheless observed to be fully reversible on annealing the sample temperature to 250 K. This recovery is attributed to changes in oleic acid passivation efficiency, and its relaxation time follows an approximate power-law relationship with the laser excitation power.

Methods

The CdSe NPLs were synthesized at high temperatures following the colloidal synthesis protocol.³² The anisotropic growth of NPLs is controlled by the addition of short chain ligand cadmium acetate during the growth and oleic acid used as a capping ligand. The morphology of the synthesized 4 monolayer (4 ML) thick CdSe NPLs is investigated from the transmission electron microscopy (TEM) images presented in Fig. 1(a). The synthesized NPLs are rectangular in size with an average thickness of \sim 1.24 \pm 0.02 nm. The room temperature optical properties of these NPLs were investigated from steady state UV-visible absorption and photoluminescence (PL) spectroscopy. The absorption spectrum shows two distinct bands at 2.43 eV and 2.58 eV, corresponding to heavy hole and light hole excitonic transitions [Fig. 1(b)]. The split-off transition is observed at 2.9 eV. The synthesized 4 ML CdSe NPLs exhibit emission at 2.42 eV with a very small Stokes shift of ~ 10 meV.

The PL measurement was done by exciting the sample with a 403 nm diode laser from coherent in an optical cryostat, where sample temperature can be controlled from 77 to 320 K. A thermo-electrically cooled electron-multiplying CCD detector from Andor Technology (iXon Ultra 897 with 512 × 512 pixel sensor) was used to record the PL signal.

Results and discussion

To study the temperature dependent emission properties of 4 ML CdSe NPLs, we excited the NPLs with the above

mentioned continuous wave laser at a constant power density of 605 mW cm⁻² at two different temperatures, 80 K and 250 K, as shown in Fig. 2(a) and 2(b), respectively. The spectra were captured at various time points during this steady state excitation. In the insets of Fig. 2(a) and 2(b), the time dependent change in the integrated PL intensity of the experimental data is shown, with spectra collected at two-second intervals for a period of several minutes. We observe that the PL intensity increases with time at 250 K, while the reverse trend is observed at 80 K.

Similar experiments were repeated at 80 K, 130 K, 160 K, 215 K, 250 K, 300 K, and 315 K with the same excitation power density of 605 mW cm $^{-2}$ [Fig. 2(c)]. At temperatures of 215 K and above, we observe an increase in the integrated PL intensity over time. This photobrightening persists up to our highest measurement temperature of 315 K, although we observe a drastic change in photobrightening at 250 K. In contrast, at low temperatures, the PL intensity decreases significantly over time.

We attribute these changes to ligand-nanoplatelet surface reconstruction and the degree of passivation, which control the quantum yield. We note that recent studies from other groups have also highlighted that ligand phase transitions and continuous laser excitation can trigger surface reconstruction. For example, Balan et al.20 demonstrated that an order-disorder transition in the ligand shell correlates with the photoluminescence changes associated with the ligand phase transition, while Wuister et al.33 showed that the capping layer not only passivates the surface but also actively participates in temperature dependent surface reconstruction. Furthermore Harvey et al. 19 investigated the behaviour of CdSe nanocrystals when exposed to laser excitation and observed changes in the bonding between the ligand and the surface over time.

At low temperatures, oleic acid is in a solid phase, which reduces its mobility and passivation efficiency. With continuous laser exposure, the interaction between the ligand and the

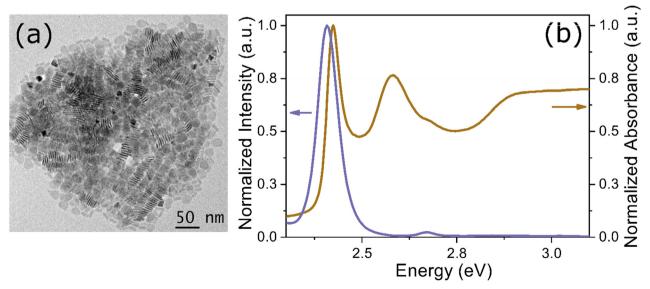


Fig. 1 (a) TEM image of 4 ML CdSe NPLs. (b) Room temperature steady-state UV-Vis absorption and photoluminescence spectra of 4 ML CdSe NPLs.

6 0 min 22 2.0 2.0 ntensity (\times 10³ a.u.) 0 min 3 min a.u.) 5 min 5 min 6.1 😅 9 10 min 10 min 60 min × 1.6 20 min 9 1.4 1.2 1.0 120 min nsity 40 min 180 min 60 mir ntensity (x 1.0 **a**) (b) 11 22 33 44 55 Time (min) 80 120 160 Time (min) 0 2.48 2.52 2.56 2.45 2.50 2.40 2.35 2.40 2.55 Energy (eV) Energy (eV) 3 Intensity (\times 10⁵ a.u.) ••••• 250K crystal Intensity (a.u.) (c) (d)130K •••• 300K 2.0 160K ····· 315K undercooled liquid gamma phase alpha phase iquid crystal 1.3 0 250 275 300 0 15 30 45 60 225

Fig. 2 Steady-state photoluminescence spectra of 4 ML CdSe NPLs at (a) 80 K and (b) 250 K temperature. The inset of (a) and (b) shows the integrated PL intensity at different time intervals at 80 K and 250 K, respectively. (c) Integrated photoluminescence intensity of 4 ML NPLs at different temperatures 80 K, 130 K, 160 K, 215 K, 250 K, 300 K, and 315 K. PL intensity was normalized to the intensity at the onset of illumination. (d) The integrated PL intensity vs. temperature. While an overall decrease in the PL intensity with increasing temperature was observed, it shows a behavior that correlates with the phases of the pure oleic acid ligand. The different phases of pure oleic acid with temperature are also marked.

surface changes over time, ¹⁹ impacting surface passivation. With lower thermal energy, more defects become active, all of which contribute to photodarkening. At high temperatures, on the other hand, the available thermal energy can perhaps support surface reconstruction and passivation. These processes may be further aided by the photons and heat received from the laser excitation. Finally, a ligand phase transition to a more mobile phase would also enhance the surface healing.

Time (min)

The thermally activated reversal of the low temperature photodarkening is further explored in Fig. 3(c) below. This is attributed to local rearrangement of the ligand molecules on the nanoplatelet surface and contributes to the overall decrease in the extent of photodarkening. In fact, the temperature of 215 K seems to impart sufficient energy to the ligands such that the low temperature photodarkening trend is reversed somewhere between 160 to 215 K. This change from photodarkening to photobrightening seems unrelated to the phase transitions in the ligand. Although oleic acid melts around 286 K, it exists in different crystalline forms, such as the 'alpha' and 'gamma' phases, below the melting point. Pluska *et al.*⁵ have presented differential scanning calorimetry (DSC) data for oleic acid and

observed changes in heat flow near the gamma phase around 250 K. The significant change in photobrightening observed around 250 K is thus linked to this phase transition. Although the bulk pure phase liquid transition temperature for oleic acid is 286 K, the ligand around the NPs is in a nanoscopic volume with a large surface to volume ratio. These may broaden the phase boundary leading to liquid-like mobility at lower temperatures. In Fig. 2(d), we have plotted the integrated PL intensity with temperature between 225-310 K. Different phases of oleic acid with temperature are also marked. In particular, a small increase in PL intensity is observed near 250 K, influenced by the oleic acid ligand phase transition.34,35 Overall, three factors, namely, thermal activation-assisted local rearrangement of the surface, laser excitation induced changes in the ligand-core interaction, and ligand phase transition all contribute to NPL surface reconstruction.

Temperature (K)

To further examine the role of oleic acid, we conducted similar measurements on a quasi type II CdSe/CdS core/shell nanoplatelet sample using the same oleic acid ligand.¹⁷ The sample preparation details for the quasi-type II CdSe/CdS core/shell nanoplatelets are provided in the ESI.† Thermal hysteresis

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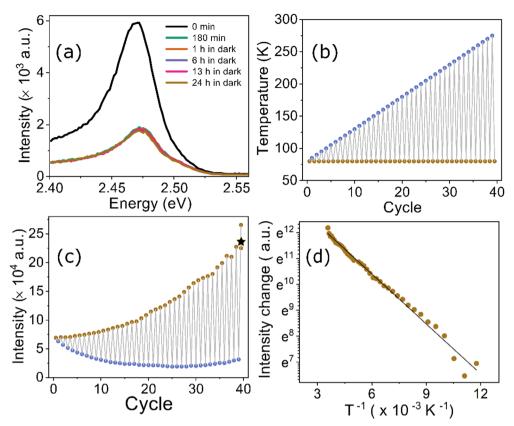


Fig. 3 (a) Stability of the photo-darkened state at 80 K. The initial spectrum at the onset of laser exposure (black). The green spectrum after three hours of exposure shows a significant decrease in PL intensity, consistent with Fig. 2(a). The laser was then switched off and the spectra were recorded every hour for more than 24 hours while the temperature was held fixed at 80 K. The photo-darkened state is seen to be extremely stable. (b)-(d) Results of the thermal annealing experiment. (b) The temperature cycling protocol, where starting with the base temperature of 80 K, the sample temperature was raised to a value of T_f with T_f increasing in steps of 5 K. (c) The corresponding integrated PL intensity from the sample after several temperature cycles. \star indicates the initial intensity, before laser exposure. (d) The change in integrated PL intensity with the inverse of the annealing temperature shows Arrhenius behavior. Here, the X-axis represents the inverse temperature, and the Y-axis shows the intensity change on a natural logarithmic scale.

in the PL intensity suggests a first order phase transition and the formation of metastable phases. We also infer the signature of phase transitions beginning at around 250 K via the observed thermal hysteresis of both CdSe [Fig. 2(d) of manuscript] and CdSe/CdS core-shell samples [Fig. S2(d), ESI†], confirming that oleic acid plays a major role in the unexpected intensity change. However, we only observed slight changes in PL intensity under continuous laser excitation [Fig. S3 of the ESI†], as the defects are primarily passivated by the CdS shell. The comparative analysis of bare CdSe and quasi-type II CdSe/CdS core/shell nanoplatelets further supports the hypothesis that this behaviour is surface-related.

Fig. 3 (a) emphasizes the stability of the darkened state at 80 K. The plot includes the initial spectrum (black) at the onset of laser exposure and the spectrum after three hours of laser exposure (green). We then switched off the continuous laser exposure and took spectra every hour for a little more than 24 hours. The laser was switched on for 100 milliseconds every hour when the spectrum was acquired. We find that this photodarkened state is indeed very stable. Once the laser was turned off after 3 hours of laser exposure, the PL efficiency remained nearly unchanged even up to 24 hours. This clearly

correlates low temperature surface damage to laser excitation. We also performed an experiment where the laser was turned off after 1.7 minutes of excitation, and the sample was kept in darkness for 24 hours. In both cases, the sample remained in a nearly identical state [Fig. S4 of the ESI†].

Fig. 3(b)-(d) summarizes the annealing induced rejuvenation of a photodarkened sample towards its pristine-like state that existed prior to the laser exposure. Starting with the photodarkened sample at 80 K [Fig. 3(a)], the sample is made to undergo multiple thermal cycles [Fig. 3(b)] where the temperature is raised to a temperature $T_{\rm f}$ and then returned to 80 K, with $T_{\rm f}$ raised by 5 K in each successive cycle. We turned off the laser during thermal cycling and waited for approximately 5 minutes before taking the spectra. The corresponding change in the integrated PL intensity is shown in Fig. 3(c), with the very initial PL intensity, prior to any prolonged low temperature laser exposure, also marked by an asterisk for reference. Note that the PL intensity incrementally recovers to beyond the initial value as the annealing temperature is raised beyond 250 K. The lower envelope in Fig. 3(c) is simply the loss of PL efficiency at high temperature, consistent with Fig. 2(d). We can further see in Fig. 3(c) that the annealing to intermediate

temperature locks the sample into a partial recovery. In Fig. 3(d), we observe that this recovery is well-fitted to $\Delta I_{\rm f}(T)/I_0 \propto \exp[-\Delta G/(k_{\rm B}T)]$ with the activation gap $\Delta G=55$ meV. Here $\Delta I_{\rm f}(T)=I_i(T)-I_0$ is the enhancement over the darkened state intensity after the $i^{\rm th}$ cycle with the annealing temperature $T_i=85$ K, 90 K,... and I_0 is the intensity corresponding to the first spectra before any cycling. The figure thus suggests that the recovery is an activated Arrhenius process with an activation barrier of 55 meV.

This thermally activated recovery quantitatively illustrates the relationship between temperature and the interaction between the oleic acid ligand and the CdSe nanoplatelet (under dark conditions). As the temperature increases, photoexcited oleic acid molecules readsorb onto the nanoplatelet surface, enhancing passivation. This suggests that approximately 55 meV of thermal activation barrier are required to be overcome to completely reverse the effects of laser excitation.

In Fig. 4, we study the temporal evolution of photodarkening under continuous exposure to laser excitation over a period of one

hour, with the sample temperature fixed at 80 K. The sample was then annealed to 300 K, brought back to 80 K, and the experiment was repeated at a different laser power density. The results of the time dependence of the integrated PL intensity are shown in Fig. 4(a). We note that photodarkening becomes more pronounced with increased laser power density. The (inverse) rate of photodarkening can be quantified by the relaxation time τ , the time when the PL intensity $I(t = \tau)$ reached a value, I(t = 0) – $e^{-1}[\{I(t=0) - I(t=1 \text{ hour})\}]$. τ shows an approximate power law $P^{-0.45}$ behaviour [Fig. 4(b)]. Furthermore, we find [Fig. 4(c)] that the value of the difference in intensity, $\Delta I = [I(t=0) - I(1 \text{ hour})]/I(t=0)$ 0) shows a strong laser power dependence for low powers but saturates at power densities around 400 mW cm⁻². In Fig. 4(d), we see that the relaxation time and the extent of photodarkening are inversely correlated until around the excitation power density of 400 mW cm⁻² where the photodarkening saturates but the relaxation time still decreases with laser power.

The observed photodarkening behaviour (power law dependence on excitation power and relaxation times on the scale of

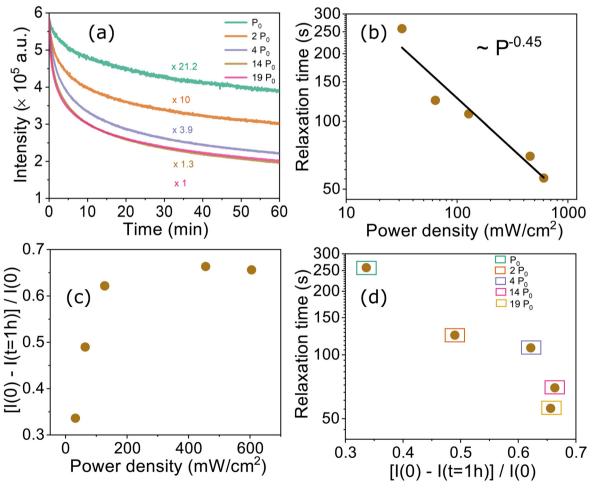


Fig. 4 (a) The time dependence of the PL integrated intensity, measured at different excitation power densities at 80 K, here $P_0 = 33.8$ mW cm⁻². The plots are multiplied by constant factors, chosen to scale the initial intensity to roughly the same value. (b) The photodarkening relaxation time tau (τ) as a function of the excitation power density. τ is defined as the time at which the integrated intensity reaches e⁻¹, the value of its asymptotic change. (c) The relative change in the integrated intensity vs. power density, where $\Delta I = [I/(t=0) - I/(t=1 \text{ hour})]/I(t=0)$. (d) τ vs. ΔI shows a strong anti-correlation with ΔI at low powers, but ΔI saturates at higher power.

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minutes) suggests that it results from laser excitation gradually altering the interaction between the ligand and the nanoplatelet over time. Additionally, the saturation of photodarkening with increasing laser power (Fig. 4(a) and (c)) indicates that as the power increases, oleic acid detaches more quickly from the core, and after reaching a certain power, the detachment is complete and thus the intensity saturates. The photodarkening relaxation time τ as a function of the excitation power density shows a power law behaviour with an exponent of 0.45, which is related to the power-dependent ligand desorption from the surface. Note that this power dependence is quite different from the Auger ionization process, which shows a quadratic dependence on laser excitation power.³⁶

Conclusions

In this work, we have demonstrated that laser excitation of CdSe nanoplatelets results in photodarkening at temperatures below 215 K, while photobrightening occurs at temperatures of 215 K and above. This behaviour is attributed to modifications in the surface-ligand interaction, which is influenced by the changes in the oleic acid ligand used for capping. Surface reconstruction is found to depend on temperature, the laser intensity, the laser exposure duration, and the phase transitions in the ligand. The photodarkened state at low temperatures remains stable for at least 24 hours when the temperature is held constant and the laser is turned off. However, this photodamage can be systematically reversed by annealing the sample to 250 K. The recovery process is thermally activated, following an Arrhenius-type behaviour, with an activation gap of 55 meV. A further large magnitude photobrightening was observed upon laser excitation around 250 K. This is correlated to enhanced ligand mobility and improved healing during the phase transition to the liquid state. These findings are valuable for applications involving laser excitation, such as solar power systems and light-emitting devices. The phase transition of different ligands in nanoplatelets will be examined in future studies. We hope that this work will serve as an initial exploration into the effects of laser-induced surface reconstruction influenced by ligand phase transitions and temperature in nanoplatelets.

Conflicts of interest

The authors have no conflicts to disclose.

Data availability

Data for this article, including text files are available at Zenodo at https://doi.org/10.5281/zenodo.15250701.

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References

- 1 B. Bai, C. Zhang, Y. Dou, L. Kong, L. Wang, S. Wang, J. Li, Y. Zhou, L. Liu and B. Liu, et al., Atomically flat semiconductor nanoplatelets for light-emitting applications, Chem. Soc. Rev., 2023, 52, 318-360.
- 2 J. Yu and R. Chen, Optical properties and applications of two-dimensional CdSe nanoplatelets, InfoMat, 2020, 2,
- 3 S. Singh, R. Tomar, S. Ten Brinck, J. De Roo, P. Geiregat, J. C. Martins, I. Infante and Z. Hens, Colloidal CdSe nanoplatelets, a model for surface chemistry/optoelectronic property relations in semiconductor nanocrystals, J. Am. Chem. Soc., 2018, 140, 13292-13300.
- 4 B. T. Diroll, B. Guzelturk, H. Po, C. Dabard, N. Fu, L. Makke, E. Lhuillier and S. Ithurria, 2D II-VI semiconductor nanoplatelets: From material synthesis to optoelectronic integration, Chem. Rev., 2023, 123, 3543-3624.
- 5 H. Jung, N. Ahn and V. I. Klimov, Prospects and challenges of colloidal quantum dot laser diodes, Nat. Photonics, 2021, **15**, 643-655.
- 6 M. A. Boles, D. Ling, T. Hyeon and D. V. Talapin, The surface science of nanocrystals, Nat. Mater., 2016, 15, 141-153.
- 7 S. Ithurria, M. Tessier, B. Mahler, R. Lobo, B. Dubertret and A. L. Efros, Colloidal nanoplatelets with two-dimensional electronic structure, Nat. Mater., 2011, 10, 936-941.
- 8 Y. Shirasaki, G. J. Supran, M. G. Bawendi and V. Bulović, Emergence of colloidal quantum-dot light-emitting technologies, Nat. Photonics, 2013, 7, 13-23.
- 9 T. K. Das and S. Ganguly, Revolutionizing Food Safety with Quantum Dot-Polymer Nanocomposites: From Monitoring to Sensing Applications, Foods, 2023, 12, 2195.
- 10 Q. Xu, Y. Niu, J. Li, Z. Yang, J. Gao, L. Ding, H. Ni, P. Zhu, Y. Liu and Y. Tang, et al., Recent progress of quantum dots for energy storage applications, Carbon Neutrality, 2022, 1, 13.
- 11 M. Pelton, Carrier dynamics, optical gain, and lasing with colloidal quantum wells, J. Phys. Chem. C, 2018, 122, 10659-10674.
- 12 A. Dutta, A. Medda and A. Patra, Recent advances and perspectives on colloidal semiconductor nanoplatelets for optoelectronic applications, J. Phys. Chem. C, 2020, 125, 20-30.
- 13 C. Rodà, A. Di Giacomo, L. C. Tasende Rodríguez, J. Leemans, Z. Hens, P. Geiregat and I. Moreels, Colloidal CdSe/CdS Core/Crown Nanoplatelets for Efficient Blue Light Emission and Optical Amplification, Nano Lett., 2023, 23, 3224-3230.
- 14 M. Sharma, S. Delikanli and H. V. Demir, Two-dimensional CdSe-based nanoplatelets: their heterostructures, doping,

photophysical properties, and applications, *Proc. IEEE*, 2019, **108**, 655–675.

- 15 Y. Guo, F. Gao, P. Huang, R. Wu, W. Gu, J. Wei, F. Liu and H. Li, Light-emitting diodes based on two-dimensional nanoplatelets, *Energy Mater. Adv.*, 2022, **2022**, 9857943.
- 16 J. F. Specht, R. Scott, M. C. Castro, S. Christodoulou, G. H. Bertrand, A. V. Prudnikau, A. Antanovich, L. D. Siebbeles, N. Owschimikow and I. Moreels, *et al.*, Size-dependent exciton substructure in CdSe nanoplatelets and its relation to photoluminescence dynamics, *Nanoscale*, 2019, 11, 12230–12241.
- 17 A. Dutta, A. Medda, S. Ghosh, S. Sain and A. Patra, 2D CdSe/ CdS Core-Shell Nanoplatelets for High-Performance Photodetectors, ACS Appl. Nano Mater., 2022, 5, 11679–11688.
- 18 A. Dutta, A. S. Almutairi, J. P. Joseph, A. Baev, A. Petrou, H. Zeng and P. N. Prasad, Exploring magneto-optic properties of colloidal two-dimensional copper-doped CdSe nanoplatelets, *Nanophotonics*, 2022, 11, 5143–5152.
- 19 S. M. Harvey, J. H. Olshansky, A. Li, S. Panuganti, M. G. Kanatzidis, J. T. Hupp, M. R. Wasielewski and R. D. Schaller, Ligand Desorption and Fragmentation in Oleate-Capped CdSe Nanocrystals under High-Intensity Photoexcitation, *J. Am. Chem. Soc.*, 2024, 146, 3732–3741.
- 20 A. D. Balan, J. H. Olshansky, Y. Horowitz, H.-L. Han, E. A. O'Brien, L. Tang, G. A. Somorjai and A. P. Alivisatos, Unsaturated ligands seed an order to disorder transition in mixed ligand shells of CdSe/CdS quantum dots, *ACS Nano*, 2019, 13, 13784–13796.
- 21 J. J. Calvin, A. B. Sedlak, A. S. Brewer, T. M. Kaufman and A. P. Alivisatos, Evidence and structural insights into a ligand-mediated phase transition in the solvated ligand shell of quantum dots, *ACS Nano*, 2024, **18**, 25257–25270.
- 22 M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. Macklin, J. Trautman, T. Harris and L. E. Brus, Fluorescence intermittency in single cadmium selenide nanocrystals, *Nature*, 1996, 383, 802–804.
- 23 C. Meerbach, R. Tietze, S. Voigt, V. Sayevich, V. M. Dzhagan, S. C. Erwin, Z. Dang, O. Selyshchev, K. Schneider and D. R. Zahn, *et al.*, Brightly luminescent core/shell nanoplatelets with continuously tunable optical properties, *Adv. Opt. Mater.*, 2019, 7, 1801478.
- 24 S. F. Lee and M. A. Osborne, Brightening, blinking, bluing and bleaching in the life of a quantum dot: friend or foe?, *ChemPhysChem*, 2009, **10**, 2174–2191.
- 25 X. Brokmann, J.-P. Hermier, G. Messin, P. Desbiolles, J.-P. Bouchaud and M. Dahan, Statistical aging and

- nonergodicity in the fluorescence of single nanocrystals, *Phys. Rev. Lett.*, 2003, **90**, 120601.
- 26 I. Chung and M. G. Bawendi, Relationship between single quantum-dot intermittency and fluorescence intensity decays from collections of dots, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, 70, 165304.
- 27 J. J. Peterson and T. D. Krauss, Photobrightening and photodarkening in PbS quantum dots, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3851–3856.
- 28 C. Liu, Y. K. Kwon and J. Heo, Temperature-dependent brightening and darkening of photoluminescence from PbS quantum dots in glasses, *Appl. Phys. Lett.*, 2007, 90, 241111.
- 29 T. Uematsu, J. Kimura and Y. Yamaguchi, The reversible photoluminescence enhancement of a CdSe/ZnS nanocrystal thin film, *Nanotechnology*, 2004, **15**, 822.
- 30 N. Korsunska, M. Dybiec, L. Zhukov, S. Ostapenko and T. Zhukov, Reversible and nonreversible photo-enhanced luminescence in CdSe/ZnS quantum dots, *Semicond. Sci. Tech.*, 2005, 20, 876.
- 31 A. Y. Nazzal, L. Qu, X. Peng and M. Xiao, Photoactivated CdSe nanocrystals as nanosensors for gases, *Nano Lett.*, 2003, 3, 819–822.
- 32 S. Ithurria, G. Bousquet and B. Dubertret, Continuous transition from 3D to 1D confinement observed during the formation of CdSe nanoplatelets, *J. Am. Chem. Soc.*, 2011, 133, 3070–3077.
- 33 S. F. Wuister, A. Van Houselt, C. de Mello Donegá, D. Vanmaekelbergh and A. Meijerink, Temperature antiquenching of the luminescence from capped CdSe quantum dots, *Angew. Chem.*, *Int. Ed.*, 2004, 43 3029–3033.
- 34 B. Brozek-Pluska, J. Jablonska-Gajewicz, R. Kordek and H. Abramczyk, Phase transitions in oleic acid and in human breast tissue as studied by Raman spectroscopy and Raman imaging, *J. Med. Chem.*, 2011, 54, 3386–3392.
- 35 F. Pi, F. Kaneko, H. Shinzawa, M. Suzuki, M. Iwahashi and Y. Ozaki, Temperature dependence of structure and dynamic properties of oleic acid γ and α phases studied by FTIR spectroscopy, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 403–412.
- 36 D. Chepic, A. L. Efros, A. I. Ekimov, M. Ivanov, V. Kharchenko, I. Kudriavtsev and T. Yazeva, Auger ionization of semiconductor quantum drops in a glass matrix, *J. Lumin.*, 1990, 47, 113–118.