

Photoluminescence quantum yield of PbS nanocrystals in colloidal suspensions

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The absolute photoluminescence (PL) quantum yield (QY) of oleic acid-capped colloidal PbS quantum dots (QDs) in toluene is thoroughly investigated as function of QD size, concentration, excitation photon energy, and conditions of storage. We observed anomalous decrease of QY with decreasing concentration for highly diluted suspensions. The ligand desorption and QD-oxidation are demonstrated to be responsible for this phenomenon. Excess of oleic acid in suspensions makes the QY values concentration-independent over the entire reabsorption-free range. The PL emission is shown to be dominated by surface-related recombinations with some contribution from QD-core transitions. We demonstrate that QD colloidal suspension stability improves with increasing the concentration and size of PbS QDs. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Colloidal semiconductor quantum dots (QDs) are the subject of fundamental and applied research because of their unique optical properties based on the quantum confinement effect.¹ This effect reveals itself when the QD radius R is less than or comparable to that of the Bohr exciton radius a_B in the corresponding bulk material. A quantum confinement regime is called “strong,” when $R < a_e, a_h$, where a_e and a_h are the Bohr radii of electron and hole, respectively. As most of II–VI and III–V materials have small Bohr radius of holes,² very small QDs are required to achieve strong quantum confinement limit in these semiconductors. On the other hand, semiconductor QDs composed of IV–VI materials and, in particular, the lead chalcogenides PbX ($X = S, Se, Te$) offer unique access to the regime of extreme quantum confinement, for instance, bulk PbS has small direct band gap (0.41 eV), with $a_e = a_h = 10$ nm and $a_B = 18$ nm. Thus, such large Bohr radius provides strong confinement even for quite large QDs (~ 10 nm), where the influence of surface effects is less pronounced than for QDs of II–VI or III–V materials with the same level of confinement because of reduced surface-to-volume ratio.

The fundamental theoretical work on electronic structure and optical properties of PbS and PbSe QDs has been presented by Kang *et al.*³ in 1997 and the procedure of a reliable and flexible colloidal synthesis of PbSe QDs was developed in 2001.⁴ During the last decade, lead chalcogenide QDs have been investigated as potential active materials for low-cost and efficient photovoltaic devices. The tunable electronic transitions of PbX QDs from infrared to ultraviolet region are of interest for producing multi-junction solar cells, which could harvest large part of the solar spectrum. Lead chalcogenides QDs have already been successfully used in LEDs,^{5,6} lasers,⁷ solar cells,^{8–10} photodetectors,^{11–13} luminescent solar concentrators,^{14,15} and biolabeling.^{16–19} However, despite the intensive investigation it is still a challenge to synthesize

colloidal quantum dots of narrow-size distribution and well-passivated surface. To the best of our knowledge, there are currently two well-developed methods to synthesize PbS QDs. The first route is based on the injection of bis(trimethylsilyl)sulfide (TMS) in octadecene to a hot solution of lead oleate (Hines and Scholes synthesis²⁰), which offers monodisperse QDs over a broad size range (2.5–8.8 nm).²¹ Recent modifications of the method allow for synthesis of ultrasmall PbS QDs with sizes between 1 and 2 nm.^{22–24} The second route includes lead chloride (PbCl₂) and elemental sulfur (S) as precursors and oleylamine is used as a solvent (Cademartiri *et al.* synthesis²⁵). Recently, Cademartiri method was modified by adding tri-*n*-octylphosphine (TOP) to solution,²⁶ which offers available size tunability between 3 and 10 nm.

In spite of the growing number of reports about colloidal suspensions of PbS QDs, detailed knowledge of some important parameters is still missing. One of them is the photoluminescence (PL) quantum yield (QY) which characterizes quality of a luminescent material. Many PL QY set-ups have limited number of available excitation wavelengths (laser lines or lamps with band-pass filters). But this limitation is commonly considered to be acceptable as the Kasha-Vavilov (KV) rule is believed to be fulfilled (The rule states that both the luminescence spectral shape and its QY do not depend on the applied excitation wavelength²⁷). However, PL QY of QDs was found to be excitation wavelength dependent due to the size-distribution and other effects.²⁰ But there are no in-detail studies on the excitation dependence of PL QY for PbS QDs yet. Moreover, it is commonly recommended that luminescent solutions must be strongly diluted to avoid the concentration quenching. However, such dilute suspensions of QDs could suffer from instability of QDs and reveal perturbations of PL QY values. Thus, the investigation of PL QY of PbS QDs depending on the concentration of suspensions and the QD size is of immense practical importance.

The main goal of this work was to study PL QY of conventional oleic acid-capped PbS QDs in toluene for various

concentrations and over a broad excitation spectral range. We uncover and discuss some specific features of the PL QY like the abnormal increase of PL QY with concentration or violation of the KV rule.

II. INSTRUMENTATION AND MATERIALS

The oleic-acid (OA) capped PbS QDs were purchased from MK Nano (mean diameter $d = 2.4$ nm and 3.3 nm) and Strem Chemicals ($d = 3$ nm) and dispersed in toluene (Uvasol, Merck) at different concentrations. The stock suspension nominal concentrations were 60, 50, and 93 $\mu\text{M/l}$ for 2.4, 3, and 3.3 nm QD's sizes, respectively. The size and the spectral position of the first absorption peak of PbS QDs obtained from MK Nano are in agreement with the following equation:²⁸

$$E_0 = 0.41 + \frac{1}{0.0252 d^2 + 0.283 d}, \quad (1)$$

where d is the QD diameter.

Absorption and emission spectra of the three samples are presented in Fig. 1. The PbS QDs suspensions were sealed into quartz cuvettes of either the standard size of $1 \times 1 \text{ cm}^2$ (sample volume of 3 ml) or smaller $0.5 \times 0.5 \text{ cm}^2$ cuvettes (0.75 ml volume for highly concentrated samples). The absorption spectra

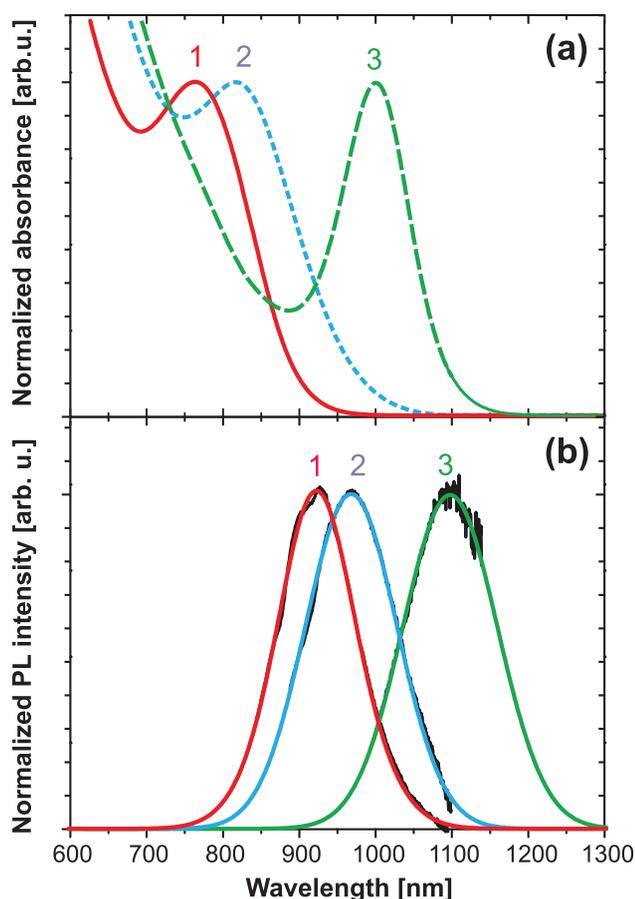


FIG. 1. Absorption (a) and photoluminescence (b) spectra of investigated samples of PbS QDs with the mean diameter of 2.4 nm (1), 3 nm (2), and 3.3 nm (3). The experimental PL spectra (black lines) are fitted by Gaussian bands in order to extend the spectrum above the detection limit at around 1100 nm.

were taken using the double-beam spectrophotometer (Specord 250, Analytik Jena) with the pure solvent as a reference sample. We have to note that toluene has some absorption features in the spectral range between 850 and 950 nm that slightly influence the measured PL spectra (see supplementary information,²⁹ Fig. S1).

For the time-resolved PL spectroscopy (TRS), we have used excitation by the diode pumped solid-state laser (MPL-F-355, Changchun Industries Optoelectronics Tech. Co. Ltd.) emitting at 355 nm (pulse duration ~ 5 ns and repetition rate 5 kHz) and detection with the photon-counting photomultiplier (H11526-20-NF, Hamamatsu) connected to a multichannel scaler (MS-300, Becker & Hickl).

The UV-stability experiment was performed by continuous irradiation with UV light from the 380-nm LED. The absorbed dose during one irradiation step was 9.8×10^{15} photons. This means the average absorption of 0.7 photon per NC for a sample which contains 1.4×10^{16} NCs.

We determined the absolute external PL QY directly by using a set-up based on an integrating sphere (IS) with diameter of 10 cm (SphereOptics GmbH). The measured cuvette was introduced from top through a square port and excited by indirect diffused light (see Fig. 2(b)). Light from IS was coupled to a silica fibre bundle whose output was imaged to an imaging spectrometer (Acton SpectraPro SP2150i, focal length $f = 15$ cm) with a deep-depletion back-illuminated CCD camera (Spec-10:400B, Princeton Instruments). The apparatus response was radiometrically calibrated in the range from 300 to 1100 nm (for details see Ref. 30). PL was excited by various LEDs emitting in the range from UV to NIR region. The PL QY was calculated as the ratio of the number of emitted photons (the difference between the investigated and the reference sample signals in the region of

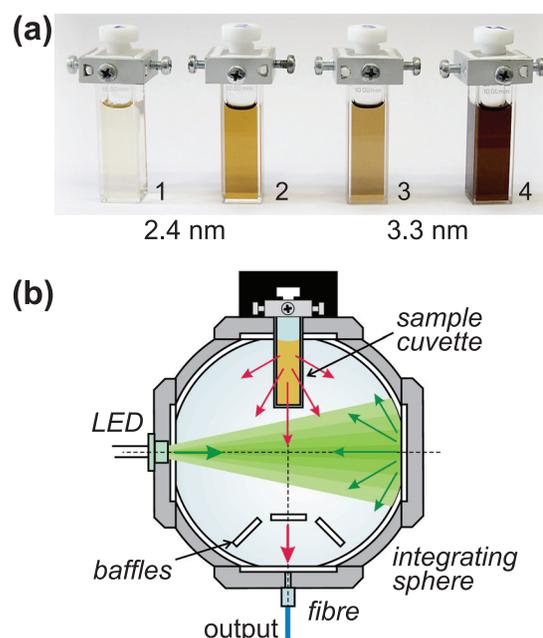


FIG. 2. (a) Suspensions of OA-capped PbS QDs in toluene with the mean diameter of 2.4 nm (1,2) and 3.3 nm (3,4) and concentrations of 1.55 $\mu\text{M/l}$ (1), 7.75 $\mu\text{M/l}$ (2), 3 $\mu\text{M/l}$ (3), and 8 $\mu\text{M/l}$ (4); (b) schematic representation of the integrating sphere set-up with an indirect LED excitation of PbS QDs samples in cuvettes.

photoluminescence) and the number of absorbed photons (integrated decrease of the excitation source signal in the sample compared to the reference)

$$QY = \frac{\sum_{em.band} \left[\frac{I_{PbS}^{em}(E_{em}) - I_{ref}^{em}(E_{em})}{C(E_{em}) \times T_{emF}(E_{em}) \times E_{em}} \right]}{\sum_{ex.band} \left[\frac{I_{ref}^{ex}(E_{ex}) - I_{PbS}^{ex}(E_{ex})}{C(E_{ex}) \times T_{exF}(E_{ex}) \times E_{ex}} \right]}, \quad (2)$$

where I^{em} and I^{ex} are the measured emission and excitation intensities for the PbS QDs solutions and reference pure toluene samples (marked by subscripts “PbS” and “ref”). C is the sensitivity spectrum of the apparatus lamp. The functions T_{exF} and T_{emF} represent transmittance spectra of filters used during acquisition of excitation and emission signal, and E_{ex} and E_{em} are the emission and excitation photon energies, respectively.³¹

III. RESULTS AND DISCUSSION

A. Excitation photon energy dependence of PL QY

PL QY of all three PbS QD samples with various concentrations was determined in a broad excitation spectral range (from about 300 nm up to an excitonic absorption band) using excitation by about 30 different LEDs. The results are presented in Figs. 3 and 4. While the absolute QY values are sample dependent, the general tendency in QY excitation spectra is the same: PL QY for the resonant photon energies (within the excitonic absorption peak) is higher than for excitation to higher energy states. It is commonly expected that PL QY of QDs decreases for larger excitation photon energies because the relaxation of generated hot carriers can take place via various non-radiative pathways related to surface and other trap states.³² We observe that for all investigated sizes of PbS QDs the non-resonantly excited PL QY is approximately linearly decreasing with increasing photon energy. Only the 3.3 nm dots reveal QY increase in the UV region.

The literature reports on excitation spectra of PL QY in PbS QDs are very rare. We can refer to the paper by Fernee *et al.*,³³ who reported on two linear regimes of QY vs. photon energy dependence for a resonant and non-resonant excitation of 2 nm PbS QDs in hexane with PL QY values close to our results on 2.4 nm PbS QDs.

B. Concentration dependence of PL QY

The concentration dependence of PL QY is extracted in Figs. 3(c) and 4(b). The QY values for big QDs (3 nm and 3.3 nm) are concentration-independent for concentrations up to 5 $\mu\text{M/l}$ (Fig. 3(c)). At higher concentrations, PL QY is reduced due to the well-known effect of reabsorption — emitted light can be reabsorbed by QDs in the region of the spectral overlap between absorption and emission. The reabsorption reveals itself in a distortion of the emission spectrum at its high-energy edge with the red-shift of the emission maximum upon increasing concentration. Moreover, the reabsorption effect is particularly pronounced for integrating sphere setups, where

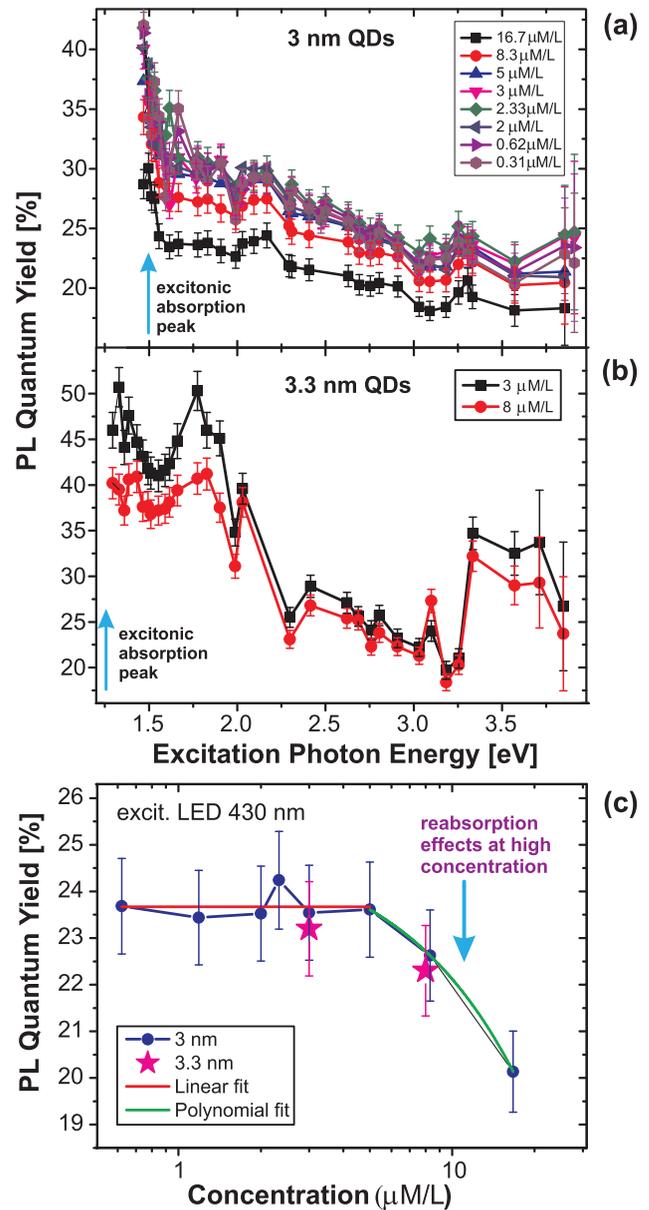


FIG. 3. PL QY dependence on the excitation photon energy ((a) and (b)) and solution concentrations (c) for 3 nm (a) and 3.3 nm (b) PbS QDs in toluene. The blue arrows indicate positions of the excitonic absorption peaks.

the mean light pass through a sample is increased by multiple reflections. To avoid this effect, the measurements should be done for sufficiently diluted suspensions of QDs or a reabsorption correction should be applied. Another motivation for avoiding too high concentrations of QDs is aggregation, which could disturb the correct determination of absorbance in some spectral regions and the contribution of QD aggregates should be considered in this case.³⁴

C. Abnormal dependence of PL QY on concentration

In the case of small PbS QDs (2.4 nm), we observe surprising decrease of PL QY with decreasing concentration (B) even for highly diluted samples ($<5 \mu\text{M/l}$, Fig. 4(b)) with negligible reabsorption. In our opinion, the most probable origin of such behaviour is the surface quality which changes with concentration in case of small QDs. Namely, the ligand

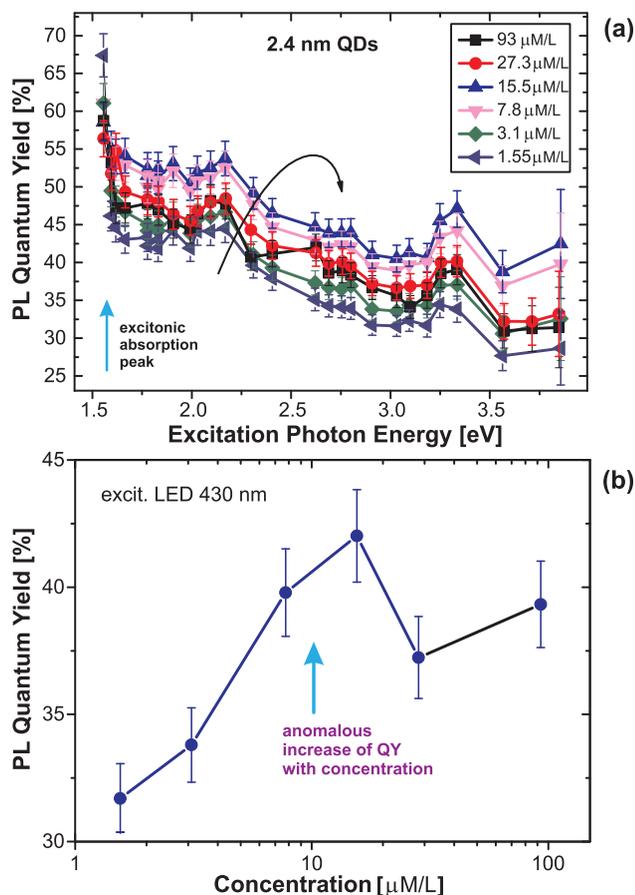


FIG. 4. PL QY dependence on the excitation photon energy (a) and solution concentrations (b) for 2.4 nm PbS QDs in toluene.

desorption and oxidation of QD surfaces can take place and affect the PL QY values.

The abnormal PL QY concentration dependence was previously reported for QDs of CdTe³⁵ and CdSe/ZnSe/ZnS³⁶ and was attributed to the ligand adsorption-desorption equilibrium. As the smaller QDs have higher surface-to-volume ratio, the probability of partial ligand desorption at lower QD concentrations is higher for small QDs than for big ones. When QDs become less protected from their environment, the reduction of PL QY is observed. This effect could be, in general, expected for QDs consisting of a semiconductor core and surface-bound ligands that are non-covalently bound to the particle surface.³⁴ The second argument why smaller QDs could be more sensitive to the concentration of suspension is the size-dependence of oxidation itself. It was reported³⁷ that larger PbS QDs are more robust against oxidation compared to smaller QDs, which effect was attributed to the trap site oxidation effects. This behaviour is in agreement with our experiment and will be discussed in Sec. III D.

Thus, relatively small PbS QDs can be considered as stable particles only at sufficiently high concentrations.³⁸ Obviously, for very high QD concentrations the PL-reabsorption effect reduces PL QY values of small PbS QDs as well as for bigger QDs (Figs. 3 and 4). That points out the importance of measuring PL QY for different concentrations to reveal and correct for possible ligand desorption and PL

reabsorption effects. However, for larger PbS QDs the ligand desorption effects may be observed only at very low concentration,³⁵ where QY measurements become difficult. The concentration-selective ligand desorption dynamics has been reported as the main parameter determining the photo-oxidation process of 3.7 nm PbS QDs. The effect was well pronounced for low QD concentrations only (0.06–0.3 μM/l). To support the idea of ligand desorption, we have prepared two set of 3.3 nm PbS QD suspensions with different concentrations. Into one set we added 10 μl of OA in toluene (1:4 OA in toluene, i.e., 2 μl of pure OA, Sigma Aldrich). As expected, a small reduction of QY has been observed for concentrations lower than 0.5 μM/l (see Fig. S2 in supplementary information²⁹). On the other hand, for samples with added OA we observed almost no decrease of QY with decreasing concentration, so indicating that the ligand desorption from surfaces of QDs can be the origin of the abnormal QY concentration dependence.

D. Degradation of optical properties

Previous reports^{24,26,39} about lead chalcogenide QDs reveal the dependence of QD stability not only on particle size, concentration, ligand, solvent, and conditions of storage (darkness, room light, or UV exposure)⁴⁰ but also on other parameters such as nanocrystal surface geometry and shape²³ and synthesis method.²⁶ While the PbS QDs synthesized by modified Cademartiri method are air-stable over the entire available size range,²⁶ the QDs produced by Hines method²⁰ are commonly considered as air-stable only for rather small QD sizes,^{23,39} The enhanced stability of QDs synthesized by the Cademartiri method can be due to the PbCl_x passivation layer that prevents QD surface from oxidation.^{26,41}

In contrast, our PbS/OA QDs reveal better air-stability for larger QDs. After 13 days of storage, the 2.4 nm QDs demonstrate blue shift of 12 nm for 7.75 μM/l, while for the 3.3 nm QDs it is only 4 nm for 8 μM/l (Fig. 5). The same size-dependent stability was reported also for PbS/OA³⁷ and CdTe⁴² QDs but reports on concentration-dependent stability of PbX (X = S or Se) QDs are very scarce.^{40,43}

In Fig. 5(b), we present the concentration dependence of air-stability of 2.4 nm and 3.3 nm PbS QDs stored in darkness. One can see that the stability of suspensions is improving with increasing concentration for both QD sizes. This observation can be understood in the framework of the ligand adsorption-desorption equilibria hypothesis mentioned in Sec. III C: for less concentrated samples, the ligand is less stable and higher fraction of QD surface is oxidized. Moreover, we observe (Fig. 6) more pronounced concentration-dependence of QD stability for small QDs, which have higher ligand desorption probability and so becomes more prone to oxidation. These results are in agreement with paper 43 but in contrast to Ref. 40 related to PbSe QDs.

The process of QD surface oxidation and ligand degradation can be accelerated by illumination with UV light (see Fig. S3 and supplementary information).

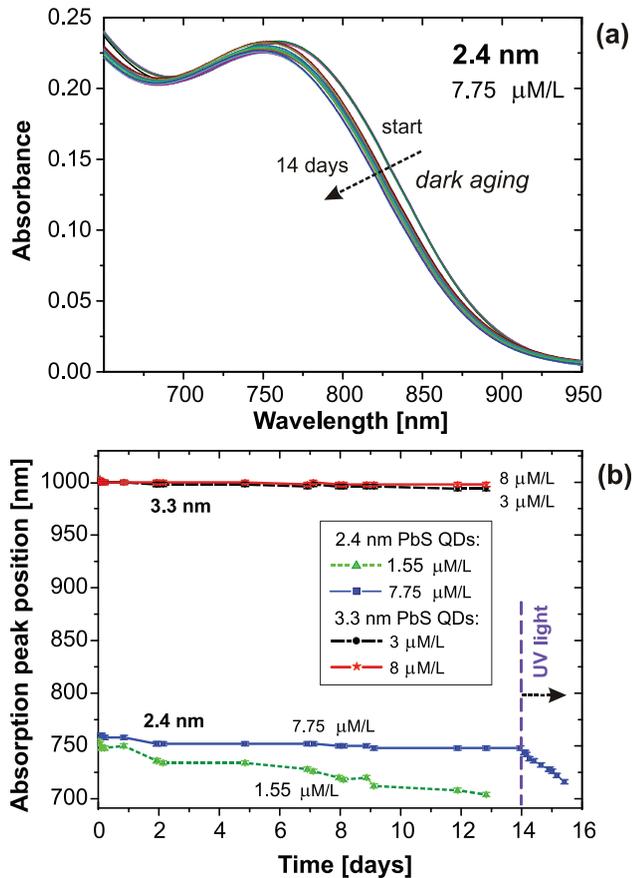


FIG. 5. (a) Optical evolution of the first absorption peak of 2.4 nm PbS QDs stored in darkness for 13 days. (b) The shift of absorption peak for 2.4 nm (\blacktriangle , \blacksquare) and 3.3 nm (\bullet , \star) OA-capped PbS QDs in toluene at different concentrations stored in darkness. The UV light marked region is related to the storage regime under continuous UV light illumination which accelerates degradation of PbS QDs.

E. The origin of PL

More information on the origin of PL in PbS QDs can be obtained from time-resolved PL experiments that could reveal a single- or multiple-component decay, depending on charge-transfer and relaxation processes. PL decay kinetics of the 2.4 nm QDs with different concentration are shown in Fig. 6(a). All the kinetics are well fitted by a biexponential decay

$$I_{PL} \sim A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (3)$$

with τ_1 and τ_2 in the range of 40–215 ns and 415–1240 ns, respectively. Even if such form of PL decay is quite typical for colloidal QDs,⁴⁴ many papers on PbS QDs report on a single-exponential decay.^{21,22,45,46} However, two papers^{21,46} present analytical models which predict the biexponential PL decay of PbS QDs. Ushakova *et al.*²¹ derived the shorter lifetime value of about 100 ns for 3 nm diameter of PbS QDs in tetrachloromethane including the increase of lifetime by factor 11 due to the dielectric screening. Similar screening factor $\varepsilon \sim 9.5$ for toluene solvent can be calculated by Eq. (4)

$$\varepsilon = \frac{(\varepsilon_1 + 2\varepsilon_2)}{(3\varepsilon_2)^2}, \quad (4)$$

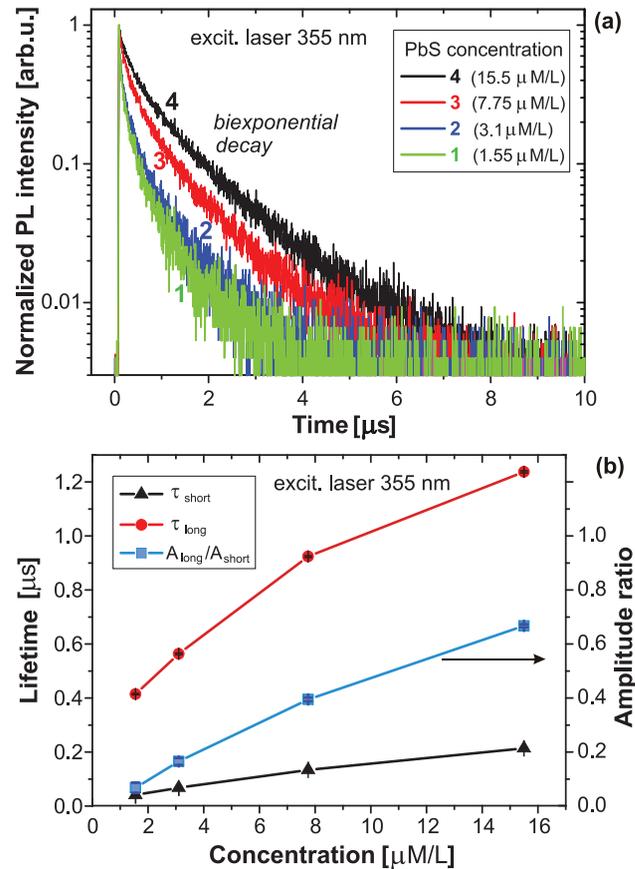


FIG. 6. (a) Time-resolved PL decay of 2.4 nm PbS QD suspensions of different concentrations. (b) The concentration dependence of long and short lifetime components as well as their amplitude ratio.

where $\varepsilon_1 = 17.2$ and $\varepsilon_2 = 2.38$ are dielectric constants for toluene and PbS, respectively. Taking into account that most of theoretical models use bulk material parameters for calculation and the fact that toluene is absorbing light in the emission range of our QDs (see supplementary information²⁹), we found good agreement of our fast lifetime components with theoretically predicted ones. We suppose that this fast τ_1 component appears as the radiative recombination of excited carriers in a QD core. To our best knowledge, there is only one paper reporting about fast lifetime component (~ 100 ns) of PbS QDs in TCE and water.¹⁶

Long PL lifetimes have been reported previously for lead selenide^{47,48} and lead sulfide^{16,22,45,46,49} QDs. Such longer lifetime component could be attributed to the recombination of spatially separated carriers in surface-localized states and core states.³³ Because of the small overlap of wavefunctions of these separated carriers, the radiative lifetime becomes much longer.²¹ Indeed, there are several papers reporting on the presence of in-gap surface states in PbS QDs.^{21,33,46,50} The large inhomogeneous line-width of PL spectra of single PbS QD could indirectly indicate on exciton trapping in surface states or defect sites.⁵¹ Defects can consist of unpassivated sulfur atoms, as it is known⁵² that oleic acid bounds only to lead surface atoms. The model of Fernee *et al.*³³ assumes that these surface states act as shallow hole traps in QDs and lie about 370 meV below the bulk semiconductor valence band-edge. However, the exact structure of surface states must be investigated separately.

Fig. 6(b) demonstrates that the amplitude ratio of longer versus shorter lifetime components is decreasing with concentration of suspension (QY). It indicates that the surface-related emission is mainly responsible for the efficient PL of our QDs, which is in contrast to the usual assignment of high QY to an efficient electron-hole recombination in a QD core. However, it was recently demonstrated that radiative surface sites could serve as efficient luminescent centers for strongly quantum confined PbS³³ or CdSe⁴⁴ QDs and does not necessarily lead to PL quenching. This is consistent with our observation of concentration-dependent surface changes. The enhanced oxidation of more diluted samples results in concomitant surface passivation that partially eliminates luminescent trap centers. Moreover, the surface quality degrades because of newly introduced non-radiative quenching defects that suppress the fraction of surface-related emission.

Both the radiative and non-radiative decay rates are decreasing as the solution becomes more diluted as it can be calculated from our QY and PL decay data using Eq. (5)

$$QY = \frac{\tau_{PL}}{\tau_r}, \quad \frac{1}{\tau_{PL}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}, \quad (5)$$

where τ_r , τ_{nr} , and τ_{PL} are radiative, non-radiative, and PL decay lifetimes, respectively. However, the non-radiative decay rate is changing more. Thus, the higher oxidation rate of QDs in low-concentrated suspensions results in larger number of non-radiative pathways introduced by oxidation products. The radiative part of decay rate is increasing most likely because of stronger contribution by core-state recombination.

F. The comparison of QY values

There are various PL QY values of PbS QDs reported in the literature that were obtained for different QY measurement

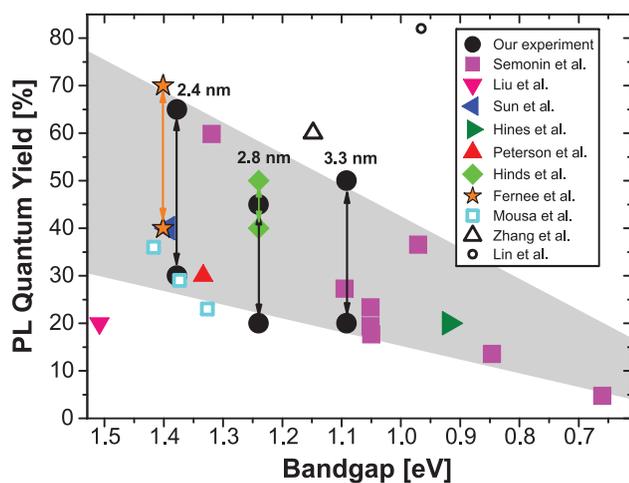


FIG. 7. Relation between PL QY and optical gap (inversely related to the QD size, see Eq. (1)). Our data are represented by black circles and literature data for PbS/OA QDs in toluene or hexane are extracted from the following papers: ■ (Ref. 53), ▼ (Ref. 55), ◀ (Ref. 56), ▶ (Ref. 20), ▲ (Ref. 51), ◆ (Ref. 57), ★ (Ref. 33), □ (Ref. 58), △ (Ref. 43), and ○ (Ref. 59). The arrows define the limits where the PL QY corresponding to a size of QD could vary depending on the excitation photon energy or solution concentration.

techniques, excitation photon energies, QD synthesis methods, QD sizes and concentrations, solvents, etc. All of these parameters are more or less important. Therefore, a systematic analysis of literature data, missing so far, is of a big importance. In Fig. 7, we present comparison of QY of PbS QDs capped by oleic acid in toluene or hexane reported in different papers. In the previous paragraphs, we have demonstrated that values of QY depend on several factors (mainly on excitation photon energy and concentration of suspensions) and can vary in a broad range, which makes the comparison of literature data difficult. In spite of this, most of PL QY values in Fig. 7 are quite systematic. The trend of decreasing PL QY with increasing QD size of PbS^{26,53} and PbSe⁵⁴ QDs observed by us and others is quite evident from Fig. 7.

IV. CONCLUSIONS

In this work, we have studied absolute PL QY of PbS/OA colloidal QDs in toluene depending on the QD size, concentration, excitation photon energies, and conditions of storage. We have demonstrated that PbS QDs violate the Kasha-Vavilov rule and pointed out that PL QY must be detected over a broad excitation spectral range instead of just one or a few excitation wavelengths. PL QY value for a given sample should be, in principle, independent on concentration in low concentrated suspensions and exhibit a decrease at high concentrations due to reabsorption. Such normal behaviour was observed for PbS QDs with the mean diameter of 3 nm and bigger for solution concentrations more than 0.5 $\mu\text{M/l}$, while an abnormal decrease with decreasing concentration was observed for lower concentration solutions. The same effect has been observed for smaller 2.4 nm PbS QDs even at much higher concentrations (up to 5 $\mu\text{M/l}$).

The size- and concentration-dependent surface modifications of QDs caused by ligand desorption and oxidation have been shown to be responsible for the abnormal concentration dependence. Thus, the larger QDs in higher concentrated suspensions proved higher stability in comparison with smaller QDs and less concentrated suspensions. Therefore, the information about the concentration of QD suspension is of crucial importance when QY values are reported. Anyway, we can propose the size-invariant optimum concentration (the least affected by artefacts) of PbS QDs for PL QY characterization to be around 5 $\mu\text{M/l}$. Moreover, the addition of extra volume of OA molecules to QD solutions reduces the ligand desorption probability from the surface of QD and the QY values become more or less concentration independent in the entire reabsorption-free concentration range. Nevertheless, the storage conditions of such samples are extremely important as the UV light illumination leads to dramatic acceleration of ligand desorption and photo-oxidation processes and exponential decrease of PL QY with time of UV exposure.

The double-exponential form of the PL decay kinetics reveals two distinct relaxation processes. The short lifetime component (up to 0.4 μs) could be attributed to the intrinsic recombination of initially populated electron-hole pairs in a

QD core. The long lifetime component (up to $\sim 1.2 \mu\text{s}$) originates from efficient surface carrier trapping, which appears to be dominant in our PbS QDs.

Our experimental results clearly point to the crucial role of surface states for relaxation processes, PL QY and stability of QDs and could facilitate the optimization of PbS QDs performance for various applications.

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