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Kinetics of Aging of Large Colloidal Quantum Dots of Lead Selenide

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Abstract

Effectiveness of passivation of large PbSe colloidal quantum dots (CQD) (first excitonic peak position 2 - 2.8 μm) using commonly used passivants is studied. The kinetics of oxidation over a period of up to more than one year is investigated. The effect of in-situ passivation with $CdCl_2$, NH_4Cl, Tetrabutylammonium Iodide (TBAI), and 3-Chloro-1-propanethiol (ClPTh), and of Solid-State Ligand Exchange (SSLE) using 3-Mercaptopriopionic Acid (MPA), TBAI, and 1,2-Ethanedithiol (EDT) is studied. Oxidation under different oxygen concentrations and aging of solutions is investigated. It is found that non-passivated CQDs oxidize, in the first two hours in air, at the initial rate of 2-5 layers a day. Passivation with $CdCl_2$ or NH_4Cl may reduce that initial rate by more than two orders of magnitude. Solid State Ligand Exchange process with TBAI as substituting ligand reduces the initial oxidation rate for non-passivated grains by an order of magnitude. For passivated materials SSLE process may add further protection, particularly when TBAI is used as substituting agent. EDT used as substituting agent apparently de-passivates grains. Under low concentration of Oxygen (<50 PPM) the oxidation rate can be reduced to about one oxidized Pb atom per grain over 10-day period for passivated and then SSLE'd films. TBAI was found to be the most effective both as in-situ passivant and as exchange ligand in SSLE process. The specific results of our investigation show, that meeting conditions of acceptable (negligent) oxidation (for some specific applications) may be feasible with moderately stringent technical requirements. Long term stability of devices, using typical passivation and SSLE methods, would require encapsulation.

Keywords: PbSe; colloidal quantum dots; aging; passivation

Introduction

Colloidal quantum dots (CQD) are a subject of interest for scientists and engineers due to the materials' tunability of their optical properties. A relatively simple material synthesis and processing of film procedures offer low-cost fabrication of devices. Most efforts are being put into application of quantum dots for solar cells using Pb-based materials [1-8], with primary focus being on PbS [1-5], and more recently also on PbSe quantum dots [3,6-9]. PbSe has the advantage over PbS in larger Bohr radius (which enhances carrier transport in the CQD films) and in higher MEG [7] (which could increase exciton generation). An advantage of CQDs of PbSe over those of PbS is in their potential applications for photodetection in the range beyond 2 μm [10,11]. A major disadvantage of using those quantum dots in photonic devices is their propensity for aging (which increases the concentration of carrier traps) [6,12]. The oxidation aging is enhanced in larger grains, which have well developed (100) facets which are self-passivated and thus more prone to oxidation [1,13]. At least some improvement in passivation against oxidation for PbS and PbSe grains (shown either directly by the stability of the position of the excitonic peak or by improvement in the device performance) was reported [2,6,7,9,12,14-17]. In this paper we present a study on the kinetics of oxidation of outer layers of the CQD grains and the effect of typical passivants on aging of films of large ($\lambda_{exc} > 2$ μm) quantum dots of PbSe to evaluate the capabilities and limitations of typical passivants reported in the literature. We investigated the effectiveness of several in-situ passivants used for PbS and PbSe CQDs: $CdCl_2$ [18,19], NH_4Cl [9,11,12,20], Tetrabutylammonium Iodide (TBAI) [15], and 3-Chloro-1-propanethiol (ClPTh) [4]. We also investigated aging of CQD films after application of Solid-State Ligand Exchange (SSLE) procedures using commonly used substituting ligands: 3-Mercaptopriopionic Acid (MPA) [21], Tetrabutylammonium Iodide (TBAI) [2,9,19,22], or 1,2-Ethanedithiol (EDT)

[7,10,20,21]. The effect of the concentration of oxygen in the environment and aging in solutions were also investigated.

Results and Discussion

(For simplicity, in the following text, the first excitonic absorption peak will be referred to as "absorption peak". Similarly, CQDs of PbSe will be referred to simply as "quantum dots" or "QDs", and films of quantum dots of PbSe as "films".)

Oxidation of CQDs has two major effects on the absorption spectra of the material, as illustrated in Fig. 1 for a sample of PbSe film immediately after synthesis and after a week's exposure of the film to the air.

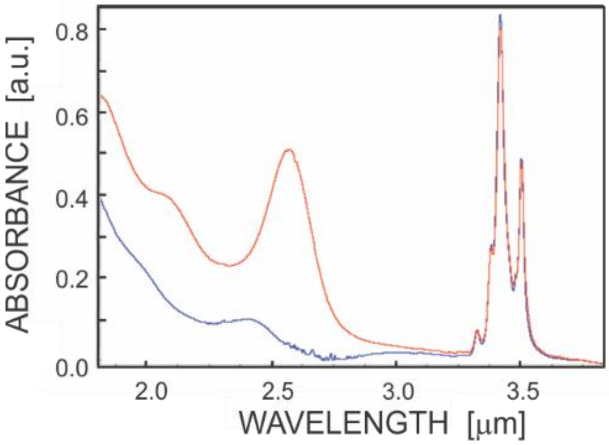

Fig. 1 Absorption spectra of non-passivated CQDs of PbSe right after synthesis and purification (red curve) and after a week's exposure to the air (blue curve).

The blue shift of the first excitonic absorption peak seen in Fig. 1 is due to reduction of the size of the PbSe grain upon oxidation. Reduction in the magnitude of the excitonic peak is apparently due to non-discrete absorption by oxidized Pb on the grains surface.

Fig. 2 shows the rate of change of the absorption peak position with time for non-passivated films with thicknesses of 75 and 900 nm. The figure shows that the rate of diffusion of oxygen thru the film is faster than the kinetics of oxidation, thus our results can be regarded as not sensitive to the film thickness.

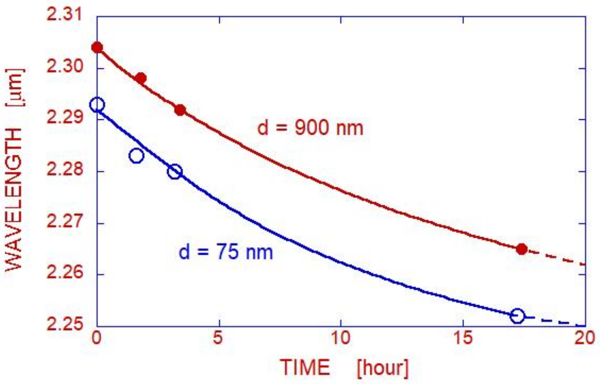

Fig. 2 Change of the position of the absorption peak with time for two films of non-passivated QDs.

We investigated the dynamics of oxidation of the external layer(s) of PbSe grains vs. time for different in-situ passivants and SSLE procedures. The analysis was based on the above illustrated change of the absorption properties of the material with time. Representative results of this investigation are shown in Figures 3 thru 12.

Oxidation rate for non-passivated films is shown in Fig. 3a. There is a strong blue-shift in the first hours of exposure to the air. Typically, in the first two hours the shift of the absorption peak position corresponds to the oxidation rate of 0.5 and 2 grain surface molecular layers per day for grains with absorption wavelength of 2 and 2.5 mm, respectively. That difference in the rate is consistent with earlier reports that larger grains are more prone to oxidation due to their prominent (100) facets (the prominence of these facets increases with an increase in the grain size) which are protected only with self-passivation by physio-adsorbed OA ligands [1,6,12]. After four months the oxidation depth is about 2 layers.

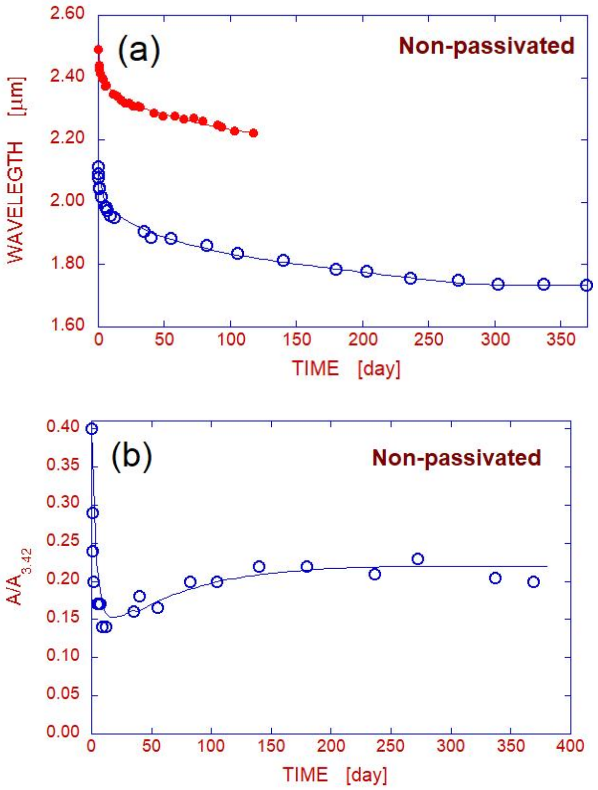

Fig. 3 Change of the absorption peak position (a) and of the relative absorbance magnitude (b) with time for non-passivated films.

Fig. 3b shows a change in the relative absorption peak magnitude with oxidation. (Due to limited reproducibility of uniformity of test samples, we focus on the ratio of the first excitonic and 3.42 mm C-H stretch absorption peak magnitudes and not on their absolute values.) The initial fast, several-fold decrease in the ratio is usually followed by a slow increase over a period of months. The increase is probably due to a slow decomposition and/or loss of oleic acid (OA) ligands from the film, and not due to an increase in the absorbance of the CQDs in the layer.

Reduction in oxidation rate upon passivation is illustrated in Fig. 4a for a range of absorption wavelengths. Effectiveness of passivation depends on the concentration of the passivant during passivation. For samples passivated at 0.01-0.02 M $CdCl_2$ in the first few hours the blue-shift rate is about 3-3.5 nm per day, which corresponds to about 0.02-0.03 layer per day. Later the rate slows down and after about a year 1-1.3 layers of the grain are oxidized. For films passivated at 0.1M $CdCl_2$ the initial oxidation rate is 3-5 times slower, and after a year the penetration rate is less than 0.1 nm per day, with 0.3 layer having been oxidized.

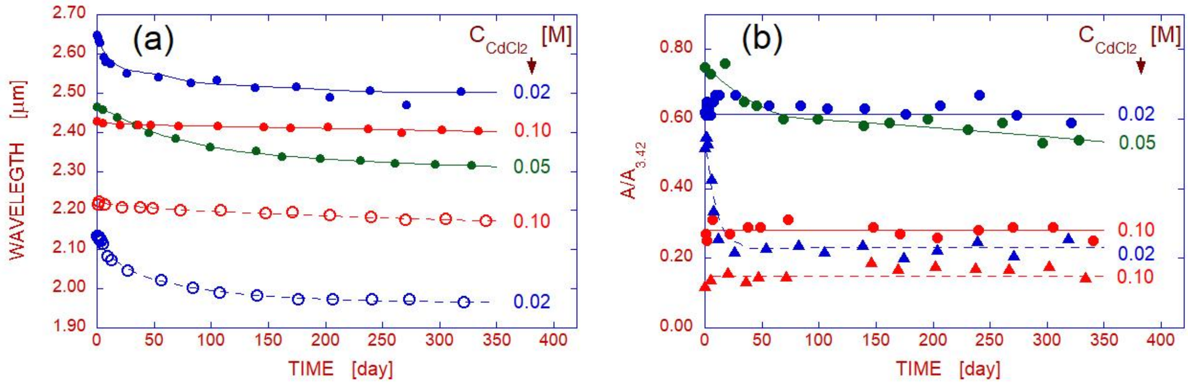

Figure 4. Change of the absorption peak position (a) and of the relative absorbance magnitude (b) with time for films passivated with $CdCl_2$. (Each color corresponds to a specific concentration.)

Adequate passivation with $CdCl_2$ improves also the material's absorbance stability, Fig. 4b. For passivation at 0.1 M $CdCl_2$ the A/A3.42 ratio is essentially stable, with a possible tendency for a slight increase with time. For lower concentrations of the passivant the film may still show initial absorbance degradation.

Oxidation of films of QDs passivated with NH_4Cl is shown in Fig. 5. As demonstrated in Fig. 5a, the blue shift is similar for all degrees of passivation. Initial blue shift rate is a few nm per day, which corresponds to penetration rate of a few hundredth of a layer per day. After about a year between 0.95 and 1.5 layer, for the shortest and longest absorption peak wavelength, respectively, is oxidized. Recommended concentration of NH_4Cl for effective passivation of small size CQDs of PbSe (λ_{exc}<1,500 nm) was reported as 0.09M [12]. For our materials best passivation was obtained already at concentrations three times smaller.

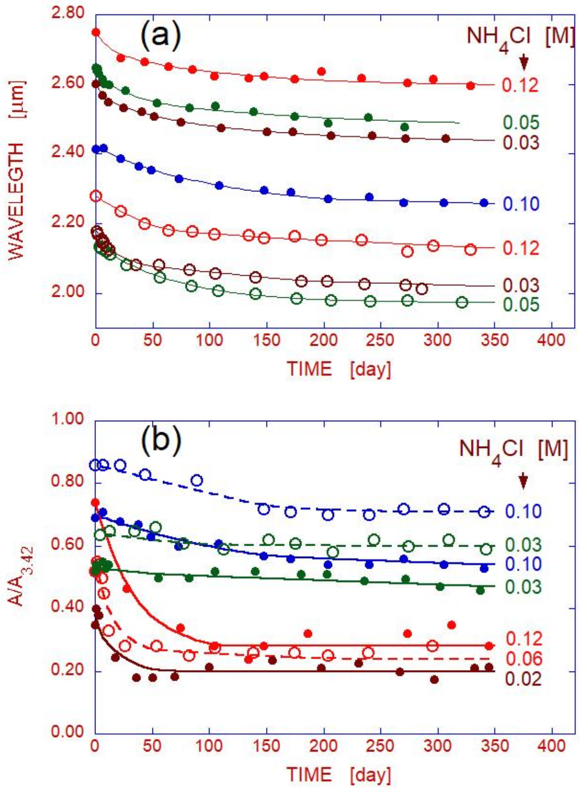

Figure 5. Change of the absorption peak position (a) and of the relative absorbance magnitude (b) with time for films passivated with NH_4Cl. Solid circles and open circles of a given color (each color corresponds to a specific concentration) are for longer and shorter wavelength, respectively.

The absorbance of Cl-passivated grains may not be steady even at a high degree of passivation, Fig. 5b. A decrease in absorbance may be very strong even for the highest degree of passivation (0.12 M). The moderate degree of passivation (0.03M) provides the most stable absorbance. In general, passivation with NH4Cl seems to be somewhat less effective than that with $CdCl_2$, which can be explained by some penetration of oxygen thru the protective layer of chlorine [1].

We found that, for samples presented in Figures 3-5, the degree of purification of the CQD solutions (and thus the amount of OA ligands in the film) does not affect the kinetics of oxidation of our materials.

SSLE process may be expected to change the kinetics of oxidation of the films. Fig. 6 shows oxidation progress after SSLE processing for films of non-passivated CQDs. The substituting ligands apparently provide some protection against oxidation. There is a significant difference in oxidation rate between films where OA ligands are replaced by MPA and those where they are substituted by TBAI ligands. In the first few hours the oxidation rate in MPA-ligand exchanged films is 0.5-1 layer per day, and after a year about 1.5 layers have been oxidized.

(This oxidation rate is about half of that observed for corresponding non-SSLE'd films, Fig. 3a.) For TBAI-exchanged films, the initial oxidation rate is about an order of magnitude lower, and after a few months the penetration depth is 2-3 times smaller than that for MPA-exchanges films. (After SSLE process the resolution and reproducibility of the C-H stretch is very poor and for those samples the analysis of the relative magnitude of the absorption peak was unreliable and is not presented.)

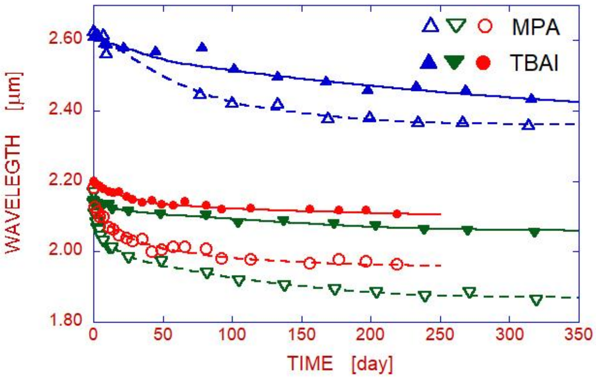

Figure 6. Change of the absorption peak position with time for non-passivated films ligand exchanged with MPA (open symbols) and TBAI (solid symbols).

Similarly, as for non-passivated materials, ligand exchange of $CdCl_2$-passivated CQD films with TBAI provides better protection against oxidation than when MPA is used: TBAI-substituted films have slower oxidation rates than those SSLE'd with MPA, Fig. 7. While films heavily passivated with $CdCl_2$ show a very slow oxidation, Fig. 4a, that protection is significantly reduced after SSLE processing: after about a year the penetration depth for materials passivated at 0.1M $CdCl_2$ is 1.8 and 1.3 layer for SSLE with MPA and TBAI, respectively, which is similar to that for non-passivated films, Fig. 6. The corresponding numbers for materials passivated at 0.02 M $CdCl_2$ are 0.6 and 0.4 layer, which is less than the degree of oxidation of the same material without SSLE processing. That is consistent with the report by Zhitomirsky et al. [4], who attributed that phenomenon to removal of some passivants during disruptive SSLE process. Apparently that disruptive process is more damaging to highly passivated films.

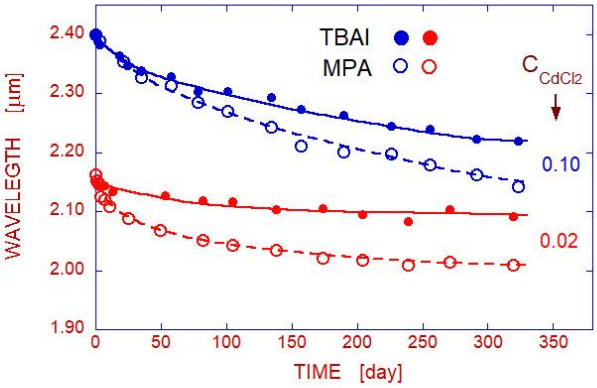

Figure 7. Change of the absorption peak position with time for films passivated with $CdCl_2$ and ligand exchanged with MPA (open symbols) and TBAI (solid symbols).

Similarly, as for QDs passivated with $CdCl_2$, films of QDs passivated with NH_4Cl where OA ligands are replaced by TBAI show a better protection against oxidation than those where MPA is used in the SSLE process, Fig 8: in the first few hours the penetration rate is higher for MPA-treated films than that after TBAI processing (approximately 0.05 and 0.02 layer/day, respectively). After a few months of air exposure, the oxidation penetrations for MPA processed films of CQDs passivated at 0.06M NH_4Cl are 1.1 and 0.8 layer for longer and shorter wavelengths, respectively. Corresponding depths for TBAI processed films are 0.9 and 0.3 layer. Similarly, as with $CdCl_2$-passivated materials, after SSLE process material with lower degree of passivation (in 0.06M solution of NH_4Cl) provides higher protection against oxidation than materials with higher degree of passivation (0.12 M). After a year the penetration depths for films with 0.12M NH_4Cl passivation and ligand exchanged with TBAI are about 1.3 layer, i.e., the same as without passivation (Fig. 6), while for less passivated materials that depth is a few times lower. Thus, excessive passivation with $CdCl_2$ or NH_4Cl is counterproductive.

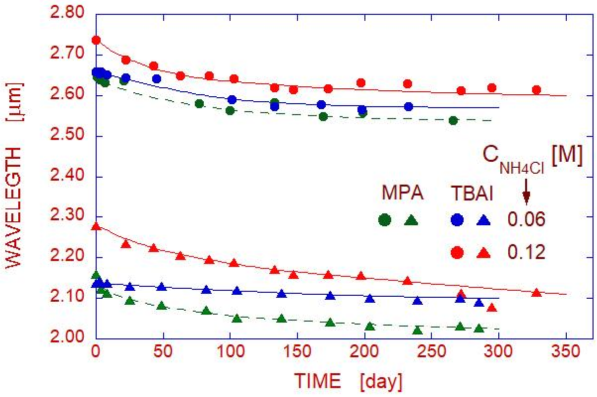

Figure 8. Change of the absorption peak position with time for films passivated with NH_4Cl and ligand exchanged with with MPA (green symbols) and TBAI (blue and red symbols).

Aging of CQDs passivated in-situ with TBAI (in the post-synthesis solution) is demonstrated in Fig. 9a (green symbols and curves). (Higher than about 0.02M concentration of TBAI in the reactor during passivation led to insolubility of the synthesis product.) The aging characteristics of TBAI-passivated CQDs is similar to that obtained for moderate (0.03M) degree of passivation with $CdCl_2$ (Fig. 4a) with penetration depth after one year approaching one layer. The absorbance of the films is very stable for months, Fig. 9b. After SSLE process the oxidation penetration rate is reduced by a factor of 3 when TBAI is used, and by 2 when MPA is used. The stability of the relative magnitude of the absorption peak with time implies that TBAI could be a passivant superior to $CdCl_2$ and that the stability is achieved at relatively low passivation level.

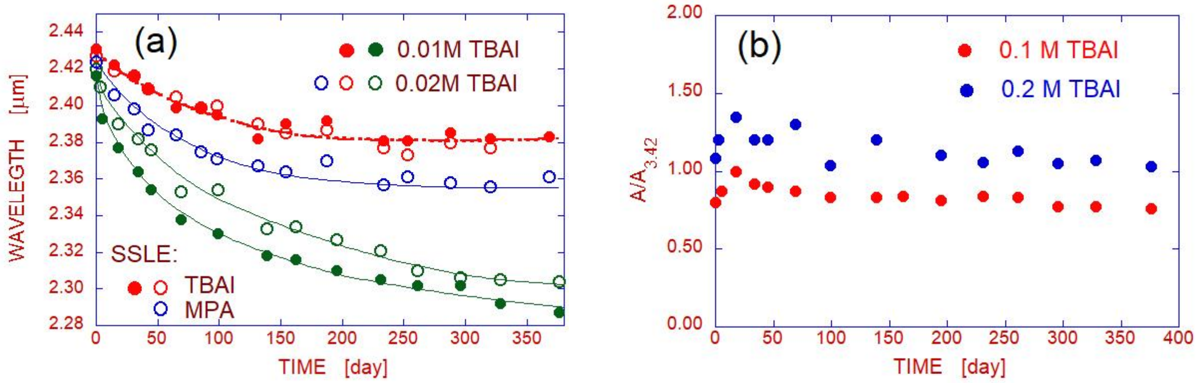

Figure 9. Change of the absorption peak position (a) and of the relative absorbance magnitude (b) with time for films passivated in-situ with TBAI. Red and blue symbols: films SSLE'd with TBAI and MPA, respectively.

Chloropropanethiol has been reported as a passivant which enhances performance of PV devices [5,23]. That can be credited to passivation of {100} facets by the short, non-site-specific thiol which withstands the removal of OA ligands during SSLE process [4,5,23]. Oxidation curves of QDs passivated with ClPTh are shown in Fig.10a (green symbols and curves). (Similarly, as with in-situ passivation with TBAI, higher than about 0.02 M concentration of ClPTh in the reactor during passivation led to insolubility of the resulting CQDs, which is probably caused by depletion of the OA ligands on the CQD surface by their excessive replacement with shorter molecules of TBAI and ClPTh and the resulting agglomeration and precipitation of the grains.) Oxidation rate of ClPTh-passivated materials is similar to those passivated using moderate concentration of CdCl2 (0.03M). Using a mixture of CdCl2 and ClPTh passivants yields similar results, Fig. 10b. (Absorbance of those materials drops fast several-fold upon oxidation.) For both ClPTh and ($CdCl_2$+ClPTh) passivated films SSLE process provides the same protection for both MPA and TBAI (red and blue symbols and curves), as opposed to samples passivated only with $CdCl_2$ or NH_4Cl, where ligand exchange with MPA leads to films oxidizing faster than those where TBAI is used (Figs. 7 and 8). Since ClPTh seems to occupy also {100} facets, those results suggests that MPA ligand is not effective in protecting those facets (which are then vulnerable to oxidation). That protection seems to be provided by ClPTh ligands [4]. Better passivation with SSLE was achieved with material of lower degree of passivation with ClPTh (0.01 M), Fig. 10a.

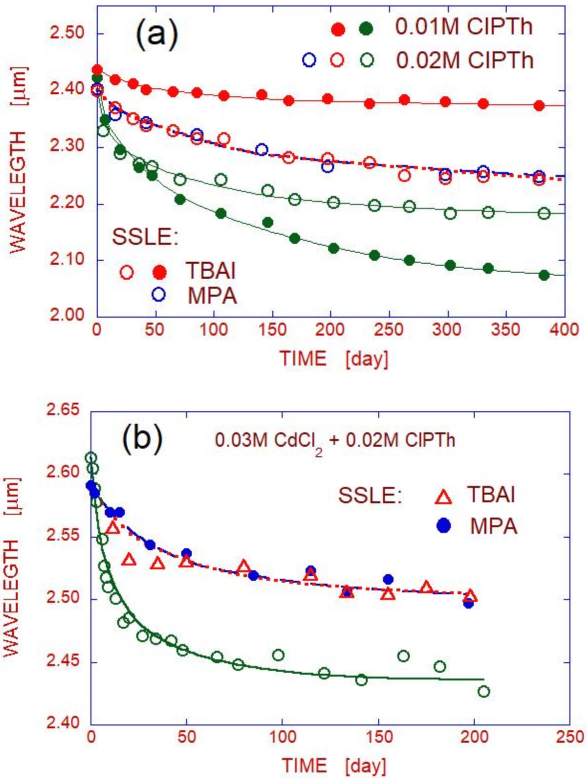

Figure 10. Change of the absorption peak position with time for films passivated with, (a), ClPTh, and (b), ($CdCl_2$ + ClPTh). Red and blue symbols: films SSLE'd with TBAI and MPA, respectively.

We tested also the effect of EDT commonly used as the substituting ligand in SSLE process. As demonstrated in Fig. 11a, EDT does not provide any protection against oxidation. That is most likely due to fast decomposition of EDT in reaction with moisture [25]. EDT even reduces the effect of passivation for films made of $CdCl_2$- or NH_4Cl-passivated materials, Fig. 11b and 11c, respectively. Such a pronounced increase in oxidation rate suggests that strong thiol groups replace chlorine passivant bonded to Pb atoms on the grain surface (and then decompose exposing the surface to oxygen).

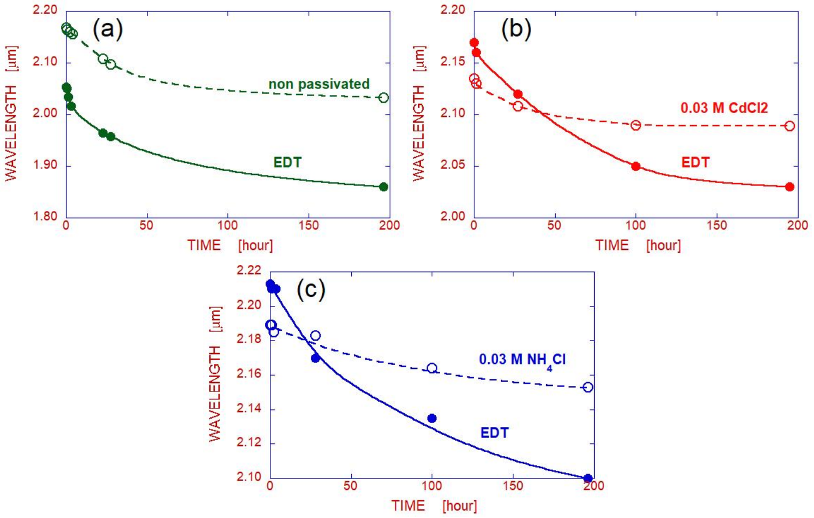

Figure 11. Change of the position of the absorption peak with time for films with different state of passivation after ligand exchange with EDT. (a), non-passivated; (b), passivated with $CdCl_2$; (c), passivated with NH_4Cl.

We studied oxidation under three different concentrations of oxygen: in the air (21% O_2), in the mixture of Argon with 5% air (1% O_2), and in high purity argon (20-50 ppm O_2). The films were made of non-passivated QDs. Fig. 12 shows change of the position of the absorption peak with time for non-treated films (black curves), and those SSLE'd with TBAI. The numbers at the curves show the blue shift for each sample after one year of exposure.

Ligand exchanged films stored in the lowest level of oxygen were found to be very stable: after more than a year of storage the position of the excitonic peak blue-shifted by only 13 nm. For our materials (average diameter of about 8.3 nm) that corresponds to about 40 oxygen atoms per grain. The samples stored in inert gas with 1% of oxygen blue-shifted by 39 nm, which corresponds to penetration depth of about 1/4th of one molecular layer. TBAI-treated film stored in the air and non-treated film stored in Argon both show a substantial oxidation, with the penetration depth of 1.5 layer, while the non-SSLE'd film oxidized to the depth of nearly 4 layers.

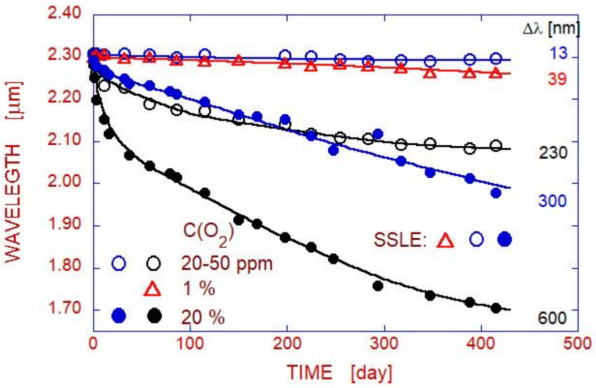

Figure 12. Change of the position of the absorption peak with time for films of non-passivated QDs. Red and blue curves: films after ligand exchange with TBAI.

More specific information in the literature on oxidation of PbSe QDs is very limited. The reports are based on stability of the absorption peak or devices over a relatively short time period (at most one month) and concern materials with wavelengths below 2 μm [6,7,9,12,14]. Typically, they show limited-time improvement in the optical properties of the materials or devices. Reports on effective passivation of PbSe CQDs with dimensions up to 12 nm in diameter, passivated in-situ with chlorine, based on direct TEM observations, were published by Pan et al. [26]. They reported to have obtained stable, non-oxidizing materials unchanged for at least two years. These conclusions were not supported by absorption measurements though. Since replacement of Se atoms in the lattice by oxygen changes the density of the material by only 22%, such a change may not be sufficient to distinguish between oxidized and non-oxidized portions of the grain in the TEM images. Thus, their conclusions require further verification.

Assuming approximately constant oxidation rate in films of passivated CQDs in the atmosphere of low concentration of Oxygen (the top two curves in Fig. 12), one day exposure may be expected to generate one oxidized site per one to three quantum dots in the film. Assuming the average space taken up by each quantum dot of 10^3 nm^3, the concentration of the grains in the film is 10^{18} per cm^3. As discussed in the literature [4], the density of detrimental traps is about one per 1000 nanocrystals. If only a moderate fraction of the QDs formed oxidized sites, the concentration of the sites is likely to be in the 10^{17} cm^{-3} range. Thus, since not all oxidation sites make deep traps, the impact of limited oxidation on carrier transport may be small. With a moderate passivation of the QDs, the initial oxidation rate can be reduced by 1-2 orders of magnitude. Further reduction in oxidation rate could be achieved by reducing the duration of exposure of the films to oxidizing atmosphere. As can be seen from the results discussed above, it may be feasible to fabricate devices based on large PbSe

CQDs with acceptable degree of oxidation by processing the materials under conditions of reduced Oxygen level and limiting the exposure of the material to the oxidizing atmosphere (and encapsulating the devices right after processing).

We studied changes of solubility of CQDs of PbSe in different solvents with time. Loss of solubility of lead chalcogenide CQDs with time has been reported my Moreels et al. [27,28]. The loss has been attributed to oxidation and resulting loss of OLA ligands with subsequent aggregation and precipitation of the grains. Stability of solutions of our CQDs in Pert, Hexane, and Octane for non-passivated and passivated materials is shown in Fig. 13a, 13b, and 13c for non-passivated, $CdCl_2$-passivated, and NH_4Cl-passivated CQDs, respectively. The labels at the curves show the type of solvent and the number of purification cycles of the samples. The absorption peak of the samples is in the 2.5 - 2.75 μm range.

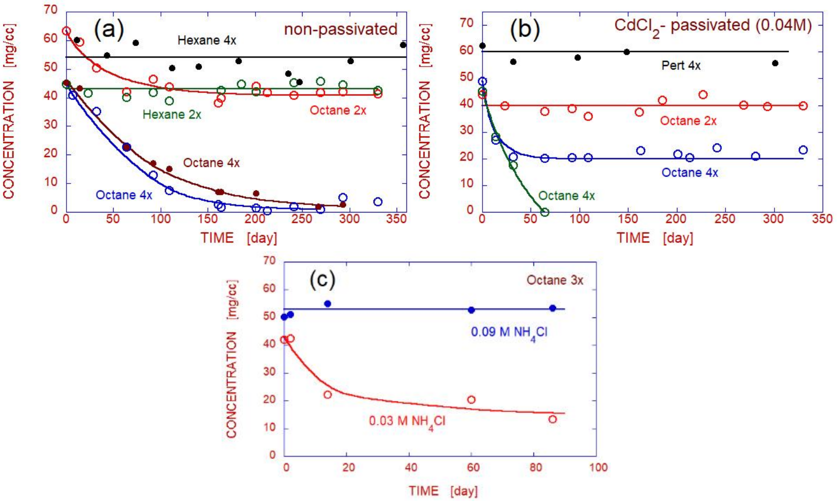

Figure 13. Change of solubility with time of solutions of QDs of PbSe for different state of passivation: (a), non-passivated; (b), passivated with $CdCl_2$; (c), passivated with NH_4Cl.

Solutions of non-passivated CQDs show instability in Octane solutions, particularly after multiple (4x) purifications, Fig. 13a. The same material purified to the same degree but suspended in Hexane or TCE is stable even after about one year of storage. CdCl2-passivated CQDs (with moderate concentration of $CdCl_2$ of 0.04M during passivation) also show limited stability of the solutions in Octane, particularly after quadruple purifications, Fig. 13b. All those samples underwent oxidations with the blue shift up to 170 nm. Extensive oxidation of the grains is indicated by a blue shift up to 700 nm (and evidenced by the reddish tint of the Selenium deposit on the walls of the containers). The curves for samples passivated with

NH_4Cl (Fig. 13c) illustrate the effect of the degree of passivation on the stability of solutions: CQDs passivated at 0.09M of NH_4Cl remain suspended in solution, while material passivated at concentration 3 times lower gradually loses its solubility (in Octane). (Corresponding samples suspended in Pert and doubly-purified QDs suspended in Octane remain stable for months.) Test solutions of CQDs passivated with ClPTh showed extended stability of solutions only with TCE as the solvent. Thus, for our samples, oxidation seems to affect long-term solubility only in case of suspensions with limited concentration of OA ligands, particularly in Octane as a solvent, and may be affected by the degree of passivation of the CQDs. While the change of concentration with time may not be an issue by itself, the tendency of some solutions to sedimentation indicates a tendency to agglomeration. Such aggregation, even below the sedimentation threshold, may be detrimental to the performance of devices and should be avoided.

Oxidation of CQDs in general, and those of PbSe in particular has profound implications for applications of the materials in photoelectric devices. Propensity of the material to oxidation may hamper the interest in devices based on (large) QDs of PbSe. For practical reasons, both short-term (like during device fabrication) and long term (during the device service) exposure to oxygen are of importance. Our results show strong oxidation of large PbSe quantum dots, and only a limited effect of their passivation by common passivants on their spectral stability. Similarly, the process of SSLE applied during device fabrication may provide only a limited further protection against passivation, if at all: SSLE with EDT seems to remove at least some of the passivants from the grain surface making the film more vulnerable to oxidation. Excessive passivation leads to reduced passivation after SSLE process. TBAI seems to be the most effective both as in-situ passivant and as a substituting ligand. In general, fabrication of devices from large-size CQDs of PbSe requires effective reduction of the oxidizing conditions (Oxygen concentration in the environment, exposition time, passivation). The specific results of our investigation show that meeting such conditions may be feasible with moderately demanding technical requirements, depending on specific applications. Long term stability of such devices, using typical passivation and SSLE methods, would require encapsulation.

The impact of oxidation, passivation, and environment on properties of devices fabricated from large (λ_{exc}>2 μm) CQDs of PbSe is under investigation and will be published in a separate paper.

Experimental

Synthesis and in-situ passivation: The syntheses were performed using a typical wet technique in non-coordinating environment described in our earlier publication [29]. The synthesized CQDs were passivated in-situ at the end stage of the growth process. For passivation with chlorine, 0.64 M NH_4Cl in outgassed Oleyamine (OLA, 90%) or 0.32M solution of CdCl2 with 0.024M TDPA in OLA were used [19]. TBAI passivation solution was 0.1M in OLA, for ClPTh 4% solution in outgassed Octadecene (ODE) was used. The reaction mixture with added passivant was stirred for 10 minutes in the temperature range of 80 - 60 °C. The molarities given in the text in the description of the passivated samples are those of the concentration of the passivant in the reaction mixture.

Solid State Ligand Exchange: SSLE process was performed using 1% solution of MPA in Methanol, 1% solution of TBAI in Methanol, or 0.01-0.2% of EDT in Acetonitrile. Concentration of the CQDs solutions was 40 mg/cc, the spinning rate was 2,500 rpm. Typically, 5 layers were deposited, with the total thickness of the film of about 200 nm.

Aging in solutions: Tetrachloroethylene (Pert), Hexane, and Octane were used as solvents. For aging in solid state, films of CQDs were obtained either by spin coating or drop casting on sapphire or quartz discs. Drop-cast layers had the thickness of about 1 μm. Test samples of non-passivated and passivated (0.04 M of $CdCl_2$) materials showed that long-term oxidation in solution follows closely the aging curves of solid film samples.

Characterization: Synthesized CQDs were characterized by their optical properties using FTIR technique (Thermo Scientific Nicolet 8700). In addition to the position of the first excitonic peak, the magnitude of the peak relative to the C-H stretch peak at 3.42 μm, A/A3.42, was determined. Concentrations of solutions (in Pert) were determined using the relation between the concentration and absorbance at 400 nm reported by Moralees et al. [30]. (Absorbances measured in Octane or Hexane solutions were about 15% lower than when Pert was used as the solvent.) For the largest grains the peak resolution is limited and gets worse with oxidation due to reduced absorbance and smaller change in L with a change in diameter, so oxidation studies were limited to the wavelengths of < 2.8 μm. Calculations of the depth of oxidation (penetration depth) were based on the relation between the (average) size of the grains and the position of the first excitonic peak [31] assuming the thickness of one molecular layer of PbSe as 0.384 nm.

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