Ultrasmall PbS quantum dots: a facile and greener synthetic route and their high performance in luminescent solar concentrators†

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Synthesis of quantum dots (QDs) with widely size-tunable optical absorption and high photoluminescence quantum yield (PL QY) via a facile route is highly desired. By introducing tributylphosphine (TBP) into a relatively green synthesis method based on the use of S, PbCl₂ and oleylamine (OLA), we conveniently synthesized ultrasmall PbS QDs with the first excitonic absorption peak wavelength as short as 705 nm, without using a glove box, which cannot be achieved by previously reported approaches, without involving smelly S precursors (such as bis(trimethylsilyl)sulfide). Such synthesized PbS QDs show narrow size distributions without any aggregation and demonstrate high PL QY in the range of 60%–90%, depending on the QD size. Based on nuclear magnetic resonance spectroscopy and X-ray diffraction investigations, TBP was found to act as the passivation ligand on the surface of QDs while simultaneously assisting the transformation of PbCl₂–OLA into more reactive Pb(OH)Cl that can directly participate the nucleation process, yielding ultrasmall PbS QDs. This new finding renders Pb(OH)Cl a very promising, new lead precursor for convenient synthesis of PbS and other lead-based QDs. We also demonstrate that the process can be readily scaled up. After synthesizing a thin CdS shell (~0.1 nm), ultrasmall core/shell QDs with a large Stokes shift (0.36 eV) and good stability were employed for fabricating near infrared (NIR) luminescent solar concentrators, which led to a record-high optical efficiency of ~1.2% at a geometric factor of ~50 (10 cm in length). The TBP route developed herein is very promising for synthesizing high quality ultrasmall QDs that have high potential in NIR-related applications.

Introduction

PbS quantum dots (QDs) have attracted increasing attention due to their size tunable optical properties in the near infrared (NIR) range arising from the quantum confinement effect. They are widely applied in optoelectronics, biological imaging and sensors.1–7 Their performance in various applications are largely determined by their size, monodispersity and photoluminescence quantum yield (PL QY), which highly depend on QD synthesis.

Various methods have been explored for synthesizing PbS QDs. Among diverse synthetic routes, the wet chemical method is well-known as an efficient low-cost path to obtain high quality PbS QDs. One of the most popular methods uses lead oxide and bis(trimethylsilyl)sulfide (TMS) as precursors and the size of PbS QDs can be tuned in the range of 2.6–7.2 nm, corresponding to first-excitonic absorption peaks of 825–1750 nm.8 However, TMS involved in the QD synthesis (denoted as the TMS route herein) shows very high reactivity and is malodorous. A glove box is always required for the manipulation of TMS for this type of synthesis, which is inconvenient, especially for industrially relevant reaction scales. Alternatively, a greener synthesis has been explored by employing elemental sulfur (S) as a replacement of TMS, as first demonstrated by Cademartiri et al. and is now widely used.9 In this scenario (defined as the PbCl₂–S route herein), PbS QDs are formed by injecting S-oleylamine (OLA) solution into the pre-heated PbCl₂–OLA solution. Although it is greener and more convenient as well as can be conducted at a larger scale, this method yields PbS QDs in a limited range of 4.2–6.4 nm as compared to the TMS route, corresponding to the first-excitonic absorption peaks of 1200–1600 nm.9 Very recently, Owen’s group developed a new method to synthesize PbS QDs with relatively small sizes (with the first-excitonic absorption peak tuned down to 850 nm), narrow size distribution and good batch to batch consistency at industrially relevant reaction scales by using thioureas as S precursor.90 However, additional procedures are needed to synthesize new precursors and a glove box cannot be completely
avoided in the synthesis. Among these methods, the PbCl₂–S route has the advantages of using “greener” and stable S source, involving convenient synthetic procedures and being cost-effective. It is worth more intense attention.

To expand the tunable range of the first-excitonic absorption peaks of PbS QDs synthesized via the facile PbCl₂–S route without the use of a glove box and TMS, Hen’s group introduced trio-n-octylphosphine (TOP) into the S precursor solution during the synthesis, by which PbS QDs with first-excitonic absorption peaks in the range of 925–2100 nm were obtained. The authors described that the major role of TOP was to form strong bond with sulfur, which led to a prolonged ripening process. Since the size-tunable optical characteristics of QDs remain one of the major driving forces for their development and practical applications, it is highly desirable to further blue-shift the first-excitonic absorption peak of PbS QDs by decreasing their sizes. Specifically, very small QDs normally have higher PL QY and optical constant, and better stability than large ones, which makes them promising in various applications, such as multijunction solar cells, light emitting diodes in “the first working window” and luminescence solar concentrators (LSCs). Additionally, the scale up of reactions, which is also of high importance, was not mentioned in this TOP-involved PbCl₂–S synthesis. Last but not least, the exploration of small QDs synthesized by the PbCl₂–S route in electronic and optoelectronic devices, such as LSCs, is quite limited to the best of our knowledge.

LSCs are composed of fluorophores embedded in a polymer matrix which acts as a wave guide. They are able to convert photons over a wide range of the solar spectrum into concentrated light in a specified manner. To the best of our knowledge, although UV-visible (Vis) QDs are widely investigated in LSCs, recent advances in the synthesis of inorganic QDs with high PL QY, size-tunable optical properties, and good chemical/photo-stability make them excellent candidates for LSC technologies. To the best of our knowledge, although UV-visible (Vis) QDs are widely investigated in LSCs, only several papers on NIR QDs can be found in this field.

Here, we introduce tributylphosphine (TBP) into the PbCl₂–S route, which leads to the important decrease in the size of PbS QDs below 2.5 nm (referred to as the TBP route herein). As a result, the first-excitonic absorption peak of PbS QDs synthesized by the PbCl₂–S method is now further extended down to 705 nm and can be tuned to cover previously not-achieved wavelength range of 705–900 nm by this method, promising for various applications. We further demonstrate that such synthesized PbS QDs show very high PL QY (60–90%), comparable to those synthesized by the TMS route and the synthesis can be easily scaled up. In addition, we discovered a surprising interaction between TBP and PbCl₂–OLA. To improve the stability of as-synthesized QDs, a thin CdS layer was further coated on PbS QDs via cation exchange. The as-prepared PbS/CdS core/shell QDs exhibit the PL QY of ~70% and Stokes shift of 0.36 eV. The LSCs using PbS/CdS core/shell QDs yield an impressive optical efficiency of 1.2% at geometric factor (G factor) ~50 (10 cm in length), among the highest values reported for QDs LSCs with similar G factor. Therefore, our work contributes to the development of both QDs and LSCs technologies in the NIR range.

**Experimental**

**Chemicals and materials**

Lead chloride (98%), OLA (technical grade, 70%), sulfur (100%), tributylphosphine (97%), cadmium oxide (99%), oleic acid, lauryl methacrylate, ethylene glycol dimethacrylate, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, cardiolig (IR 125), 1,2-dichloroethane and octadecene (ODE) were obtained from Sigma-Aldrich Inc. 4-(7-(2-Phenyl-4H-1-benzoazopyran-4-ylidene)-4-chloro-3,5-trimethylen-1,3,5-heptatrienyl)-2-phenyl-1-benzoazopyrylium perchlorate (IR 26, 97%), dimethyl sulfoxide, toluene, and ethanol were purchased from Fisher Scientific Company. All chemicals were used without any purification.

**PbS QD synthesis by TBP route**

In this route, typically 2 g PbCl₂ and 15 mL OLA were first heated at 160 ºC for 30 min under N₂ flow. Then the solution was pumped for at least 30 min to eliminate remaining water and possible impurities from reagents. Meanwhile, 20 mg of S was dissolved in 5 mL OLA and different volume of TBP was then added for synthesizing the QDs of different sizes. The S–OLA/TBP solution was subsequently injected into the Pb precursor solution after it was cooled down to 70 ºC. Finally, the reaction was quickly quenched with cold toluene after 5 s, and the obtained PbS QDs were purified several times by repeated centrifugation–dispersion processes and eventually stabilized by the addition of oleic acid ligands.

For the two-step injection, TBP of varying volume was directly introduced into the Pb precursor solution before the addition of the S–OLA solution. All other experimental conditions, including precursor preparation, reaction, purification and re-dispersion, were the same as that described above.

**PbS/CdS QD synthesis via cation exchange**

PbS/CdS core/shell QDs were synthesized by cation exchange method, following our previously reported procedures. Briefly, as-prepared ultrasmall PbS was dissolved in 20 mL toluene after purification. Appropriate amounts of Cd-OA solution (CdO dissolved in OA) was added to the PbS solution. After 3 min stirring and 6 min bubbling by N₂, the solution was reacted in a microwave oven for 8 s at 100 ºC to get the PbS/CdS with 0.1 nm CdS shell. Finally, the solution was purified by ethanol for the next step.

**LSC fabrication**

Similar to the procedures described in references, the LSCs were fabricated by embedding the TBP-route synthesized QDs into a polymer matrix. Briefly, the QDs were precipitated by adding ethanol. The monomer precursor of lauryl methacrylate and cross-linker of ethylene glycol dimethacrylate were mixed at a mass loading of approximately 20%, and then added into the...
QDs. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide was added to the resulting solution as a UV initiator. A clear solution was obtained by ultrasound treatment. Finally, the mixture was illuminated by a UV lamp for 2 h in a mold consisting of two glass slides separated by a flexible rubber spacer with thickness around 2 mm.

Characterization
Absorption spectra of the QDs were acquired with a Cary 5000 UV-Vis-NIR spectrophotometer (Varian) with a scan speed of 600 nm min$^{-1}$. Fluorescence spectra were taken with a Fluorolog®-3 system (Horiba Jobin Yvon). PL QY of QDs with emission peaks in the range of 800–1000 nm was measured using IR 125 dye (dissolved in dimethyl sulfoxide) as a reference, while the PL QY of the samples with emission peaks between 1100–1200 nm were measured using IR 26 dye (dissolved in 1,2-dichloroethane) as a reference. The size and morphology of PbS QDs were characterized by TEM (JEOL 2100F). Assuming the QDs have spherical morphology, the size histograms of corresponding samples were obtained following the equation: \( S = \pi(d/2)^2 \), where \( S \) is the areas of a single QD estimated by the imageJ software, and \( d \) is the diameter. Over 200 QDs were counted for each sample. The standard deviation was obtained by fitting the histograms using the Gaussian function. Nuclear magnetic resonance (NMR, Bruker, Avance III HD, 600 MHz) was applied to examine the surface ligand of QDs and assess the change of TBP following the reaction using toluene-D8 as a solvent. Pb/S ratio was detected by inductively coupled plasma/atomic emission spectrometry (ICP-AES, Agilent Technologie, 5100). The powder X-ray diffraction (XRD) study was carried out with a Bruker D8 advanced diffractometer using a Cu K$\alpha$ radiation source. The optical efficiency of the LSCs was measured by using an ABET2000 solar simulator at AM 1.5G (100 mW cm$^{-2}$) calibrated using a reference silicon diode.

Results and discussion
One-step TBP route synthesis of PbS QDs
Based on the widely used facile and “greener” PbCl$_2$–S route, we further developed the TBP-route to synthesize ultrasmall PbS QDs herein. All of the synthesis procedures were conveniently conducted out of the glove box. To study the effect of TBP, the synthesis was performed under identical conditions, with the only difference being the amount of TBP introduced. Briefly, TBP was first mixed with S–OLA and then this mixture was injected into PbCl$_2$–OLA solution. It was found that the optical absorption of such synthesized PbS QDs can be well controlled by varying the amount of TBP added into the S precursor solution as demonstrated in Fig. 1(a). For the purpose of straightforwardly comparing the shape, width and position of the first-excitonic absorption peaks of the QDs synthesized with different contents of TBP, all the spectra were normalized by their respective peak intensity. The exact amount of TBP used for QD synthesis and corresponding first-excitonic absorption peak positions are listed in Table S1.$\dagger$ For the TBP-free PbCl$_2$–S reaction, the shortest absorption peak wavelength of synthesized PbS QDs is limited to \( \sim 1056 \) nm, whereas the introduction of TBP largely extends the first-excitonic absorption peak range of obtained QDs to shorter wavelengths. Specifically, by increasing the volume of TBP from 10 to 40 \( \mu \)L, the first-excitonic absorption peak of QDs is blue-shifted from 1028 to 705 nm, corresponding to the QD diameter changing from \( \sim 3.4 \) to 2.2 nm (calculated from the first excitonic peak of QDs, following the previously reported method), in line with TEM observations.\footnote{The PL spectra of obtained PbS QDs are shown in Fig. 1(b), and the corresponding values of PL peak position and full width at half maximum (FWHM) of PL are summarized in Table S1.$\dagger$ Based on FWHM data, all the samples synthesized by the TBP-route show narrow size distributions. PL QY was measured according to the method described in the literature\textsuperscript{22} with 2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-1,1-dimethyl-3-(4-sulfobutyl)-1H-benz[e]indolium hydroxide (IR 125, for 2.2, 2.8 and 3.1 nm samples) or 4-(7-(2-phenyl-4H-1-benzoioxapyr-4-ylidene)-4-chloro-3,5-trimethylene-1,3,5-heptatrienyl)-2-phenyl-1-benzoioxapyrilum perchlorate (IR 26, for 3.4 nm and TBP-free samples) as the standard samples. As seen in Fig. 1(c), all of the QDs show high PL QY in the range of 60–90%, comparable to the TMS-route synthesized QDs of similar emission wavelengths.\footnote{In particular, for the TBP-samples, the PL QY increases from \( \sim 67\% \) (average value) for 3.4 nm QDs to \( \sim 83\% \) (average value) for 2.2 nm QDs, very likely due to the better passivation for smaller sized QDs.\footnote{To gain deeper insights into exciton kinetics, transient PL spectroscopy was used to measure the PL decay of the PbS QDs dispersed in toluene. Fig. 1(d) shows the typical decay curves for QDs with different diameters achieved by either the TBP-free PbCl$_2$–S route or the TBP-route. All the curves can be fit sufficiently well by a bi-exponential decay function, and the average lifetime (\( \tau \)) was calculated from two resolved lifetime components. All lifetimes are in line with those reported for PbS QDs in the literature,\textsuperscript{28} except for the 2.2 nm QDs, which show unusually long lifetime over 3 \( \mu \)s. Radiative recombination rates (\( K_{\text{rad}} \)) and non-radiative recombination rates (\( K_{\text{nrr}} \)) were then calculated using the following equations: \( \text{PL QY} = K_{\text{rad}}/(K_{\text{rad}} + K_{\text{nrr}}) \) and \( \tau = 1/(K_{\text{rad}} + K_{\text{nrr}}) \). The values of \( K_{\text{rad}} \) and \( K_{\text{nrr}} \) of all the samples are included in the inset of Fig. 1(c). The \( K_{\text{rad}} \) for all samples are more or less similar, while the trend of the large increase of \( K_{\text{nrr}} \) with QD size is well in line with the opposite trend in the PL QY of these QDs; the presence of more surface defects must be mainly responsible for the decrease of the PL QY in larger QDs.}}

The optical absorption of PbS QDs is limited to \( \sim 1056 \) nm, whereas the introduction of TBP largely extends the first-excitonic absorption peak range of obtained QDs to shorter wavelengths. Specifically, by increasing the volume of TBP from 10 to 40 \( \mu \)L, the first-excitonic absorption peak of QDs is blue-shifted from 1028 to 705 nm, corresponding to the QD diameter changing from \( \sim 3.4 \) to 2.2 nm (calculated from the first excitonic peak of QDs, following the previously reported method), in line with TEM observations.\footnote{The PL spectra of obtained PbS QDs are shown in Fig. 1(b), and the corresponding values of PL peak position and full width at half maximum (FWHM) of PL are summarized in Table S1.$\dagger$ Based on FWHM data, all the samples synthesized by the TBP-route show narrow size distributions. PL QY was measured according to the method described in the literature\textsuperscript{22} with 2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-1,1-dimethyl-3-(4-sulfobutyl)-1H-benz[e]indolium hydroxide (IR 125, for 2.2, 2.8 and 3.1 nm samples) or 4-(7-(2-phenyl-4H-1-benzoioxapyr-4-ylidene)-4-chloro-3,5-trimethylene-1,3,5-heptatrienyl)-2-phenyl-1-benzoioxapyrilum perchlorate (IR 26, for 3.4 nm and TBP-free samples) as the standard samples. As seen in Fig. 1(c), all of the QDs show high PL QY in the range of 60–90%, comparable to the TMS-route synthesized QDs of similar emission wavelengths.\footnote{In particular, for the TBP-samples, the PL QY increases from \( \sim 67\% \) (average value) for 3.4 nm QDs to \( \sim 83\% \) (average value) for 2.2 nm QDs, very likely due to the better passivation for smaller sized QDs.\footnote{To gain deeper insights into exciton kinetics, transient PL spectroscopy was used to measure the PL decay of the PbS QDs dispersed in toluene. Fig. 1(d) shows the typical decay curves for QDs with different diameters achieved by either the TBP-free PbCl$_2$–S route or the TBP-route. All the curves can be fit sufficiently well by a bi-exponential decay function, and the average lifetime (\( \tau \)) was calculated from two resolved lifetime components. All lifetimes are in line with those reported for PbS QDs in the literature,\textsuperscript{28} except for the 2.2 nm QDs, which show unusually long lifetime over 3 \( \mu \)s. Radiative recombination rates (\( K_{\text{rad}} \)) and non-radiative recombination rates (\( K_{\text{nrr}} \)) were then calculated using the following equations: \( \text{PL QY} = K_{\text{rad}}/(K_{\text{rad}} + K_{\text{nrr}}) \) and \( \tau = 1/(K_{\text{rad}} + K_{\text{nrr}}) \). The values of \( K_{\text{rad}} \) and \( K_{\text{nrr}} \) of all the samples are included in the inset of Fig. 1(c). The \( K_{\text{rad}} \) for all samples are more or less similar, while the trend of the large increase of \( K_{\text{nrr}} \) with QD size is well in line with the opposite trend in the PL QY of these QDs; the presence of more surface defects must be mainly responsible for the decrease of the PL QY in larger QDs.}}
Fig. 2 shows transmission electron microscopy (TEM) images of obtained PbS QDs. It shows that the morphology of QDs is significantly affected, from irregular to quasi-spherical, with the introduction of TBP into the reaction. It can be explained from the ligand passivation point of view as the morphology is known to be largely associated with ligand passivation. TBP herein acts as ligand, as confirmed by NMR results to be presented in the later text. Moreover, statistical histograms were obtained to further analyze the effect of TBP on QD diameter and size distribution. When the volume of TBP is zero, PbS QDs with an average diameter of 4.1 nm are obtained. With the presence of TBP in the reaction, the average diameter of PbS QDs gradually decreases with increasing volume of TBP, in agreement with the blue shift of the first-excitonic absorption peaks mentioned above. A representative high resolution (HR) TEM image of the 3.1 nm sample (inset in Fig. 2(c)) shows lattice fringes, corresponding to the (200) facet of PbS QDs and in line with their crystalline structure (Fig. S1†). Additionally, in most of the cases the size distribution is improved with the presence of TBP. In particular, the size distributions for 2.9, 3.1 and 3.6 nm QDs are significantly narrower than that of 4.1 nm QDs synthesized without TBP. From many TEM images, we also noticed that QD aggregation is effectively hindered with the presence of TBP, even for the QDs with the average diameter as small as 2.3 nm. The narrow size distribution and lack of aggregation along with high PL QY of the QDs strongly suggest that high quality of QDs have been synthesized by the TBP-route. TBP must play a significant role in determining important structural parameters, including the morphology, average diameter, size distribution and dispersity of QDs. Alkylphosphine compounds, acting as solvent and/or ligand, have been widely applied to synthesize II–VI and IV–VI QDs.\cite{11,28,29} It was reported that they can affect the nucleation reaction or crystal growth process and thereby affecting the QDs synthesis in a complicated way. Herein, we focus on a specific alkylphosphine, TBP, which was not previously explored in PbS QD synthesis, and found that it is able to considerably decrease the size of PbS QDs. Its effect on the synthesis of PbS QDs will be discussed in detail in the next section.
ICP-AES and $^{31}$P NMR spectroscopy were used to probe the surface chemistry of the TBP-route synthesized QDs, which can significantly influence their properties. Fig. 3(a) shows the results obtained in the current study and the data from the TMS route in the literature\textsuperscript{12} for comparison. We found that the Pb/S ratio of the TBP-route synthesized QDs is much lower than that reported in the literature, although the trend of the Pb/S ratios with size is similar. In all these cases of ultrasmall QDs, Pb-rich surfaces were identified. In the literature,\textsuperscript{12} the size, capping ligand and coverage of QDs and their external facets are highly correlated, and in general small-size QDs were confirmed to have more Pb-rich (111) external facets than larger ones. Our results suggest that TBP can alter the surface arrangement of Pb and S atoms, with respect to that reported in ref. 12.

To better understand the surface chemistry, $^{31}$P NMR was conducted on purified 3.1 nm PbS QDs (Fig. 3(b)). New
phosphorous resonance at −13.7 ppm was detected, indicating the presence of TBP ligands on the surface of QDs. The dramatic downfield chemical shift from around −31 ppm for pristine TBP to −13.7 ppm for TBP-QDs is ascribed to the strong interaction between TBP and S atoms on the surface of QDs. The presence of the TBP ligand on the surface could contribute to the high PL QY of the TBP-route synthesized QDs by providing extra passivation to the S-site compared to the QDs from the normal, TBP-free PbCl₂–S route and TMS-route. Controversial results regarding the role of alkylphosphines as passivating ligands have been reported in the literature. For instance, highly photoluminescent PbS QDs with a narrow size distribution can be obtained by using TOP as an additional ligand in the TMS-route. The authors attributed the improvement to the enhanced surface passivation because both Pb and S surface atoms are passivated in this case, by oleic acid and TOP, respectively. However, different result was reported by Moreels et al. In that case, TOP could not be found on the PbS QD surface. In our case, we believe that TBP (with short organic chains) has less steric effect than the analogous TOP, which facilitates its interaction with the S-sites. In addition to leading to the high PL QY, such passivation effect may induce an additional barrier for the QD growth during the synthesis. Along with the known strong binding effect between phosphines and S, the growth rate of PbS QDs decreases, leading to the observed smaller sizes.

Overall, with increasing TBP content in the S precursor solution, the first-excitonic absorption peak of synthesized PbS QDs is gradually blue-shifted from 1056 nm to 705 nm, owing to decreased QD size. TBP as the surface capping ligands could have contributed to the improved optical properties, size-distribution and affected the surface composition of TBP route synthesized QDs. In brief, the smallest QDs show the highest PL QY and longest lifetime, while QDs with the average diameter in the range of 2.9–3.6 nm have the narrowest size-distribution.

Two-step TBP route synthesis of ultrasmall PbS QDs
Motivated by the “TBP-effect”, which was able to extend the first-excitonic absorption peak of PbS QDs down to 705 nm in the one-step TBP route, we further examined the effect of TBP on PbS QD formation when it was separately injected into the PbCl₂–OLA solution followed by the S–OLA injection. When large amounts of TBP (TBP : PbCl₂ = 1 : 1 by molar) were injected, very well-defined absorption and PL spectra of the PbS QDs with peak position located at ~780 and ~890 nm were obtained (Fig. 4(a)). This two-step TBP route can also result in largely extended excitonic absorption peak as compared to PbS QDs synthesized by the normal PbCl₂–S route. The FWHM of the PL peak (160 meV) formed by this method is even narrower than what can be achieved by the TMS route for the QDs (170 meV) of similar size. The calculated PL QY of ultrasmall QDs synthesized by this two-step route is around 80%. Repeated experiments show that this two-step TBP route is highly reproducible and easily controllable. These results highlight the importance of this new, safer approach for the synthesis of ultrasmall QDs in a convenient way. As seen in the TEM image displayed in Fig. 4(b), PbS QDs with diameter around 2.5 nm have excellent dispersity without any aggregation, in good agreement with the PL result. Nevertheless, when less TBP (20 μL) was used in the two-step TBP route, bimodal absorption peaks were observed at around 973 and 1065 nm, respectively (Fig. S2†). Obviously, the presence of large amounts of TBP ligands played an important role in obtaining ultrasmall PbS QDs with a single and narrow peak. To better understand the interaction between PbCl₂–OLA and TBP, we performed additional investigations by focusing on lead precursors and TBP. Specifically two samples were prepared and compared. In the first case, PbCl₂–OLA was first prepared by heating the mixture of PbCl₂ and OLA following the same procedure used in the one-step TBP-route. The solution was then centrifuged and the obtained precipitates were washed and then dried. In the other
case, large amounts of TBP were injected into the PbCl₂–OLA solution at 70 °C followed by the same precipitation and drying operations. XRD was performed on these two samples and results are shown in Fig. 4(c), where the spectrum of commercial PbCl₂, as a reference, is also included. The diffraction pattern of PbCl₂ (JCPDS card no. 26-1150) is totally changed after reacting with OLA. Surprisingly, when TBP was involved in the reaction, the Pb compound with the crystal structure of laurionite (JCPDS card no. 74-2022) could be identified, suggesting the formation of Pb(OH)Cl.

$^{31}$P NMR spectroscopy was further employed to monitor the possible change in TBP following the reaction. Fig. 4(d) shows the NMR spectra of pristine TBP and that after Pb(OH)Cl formation, where no chemical shift was observed. As P is the

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Fig. 4  (a) Absorption and PL spectra of PbS QDs obtained by two-step injections of large amounts of TBP and then S–OLA. (b) TEM image of PbS QDs obtained by two-step injections. (c) XRD spectra of lead precursors and commercial PbCl₂. (d) $^{31}$P NMR spectra taken from pristine TBP solution and that after reaction. (e) Absorption and PL spectra and (f) TEM image of PbS QDs synthesized by Pb(OH)Cl and S–OLA.
only element in TBP that may react in this process, this finding suggests that highly likely, there is no change in the molecular structure of TBP in solution. It was reported that TBP can be considered as a catalyst in acylation reaction, and different types of alkylphosphines cause considerable changes in the product yield of PbSe QDs by different effects. Nevertheless, this is the first time that TBP was found to assist the transformation of the PbCl₂–OLA complex to Pb(OH)Cl. Since the reaction was conducted under N₂, the oxygen atom in Pb(OH)Cl may mainly come from the large excess of the commercial OLA reagent (technical grade: 70%). Although the detailed mechanism for transforming the PbCl₂–OLA complex to Pb(OH)Cl in this reaction still requires further investigations, it is already clear that the presence of TBP directly induces such a transformation, which highly likely changes the Pb–S reaction rate and leads to small QD sizes.

Pb(OH)Cl has recently been reported as a lead source to synthesize zero-dimension (0D) and 1D PbSe nanomaterials at relative low temperature, although the optical properties of such synthesized nanomaterials were not mentioned. Herein, to confirm that Pb(OH)Cl serves as the actual precursor for the formation of ultrasmall, high quality QDs shown in Fig. 4(a) and (b), precipitated Pb(OH)Cl was also employed for the QD synthesis. To do it, Pb(OH)Cl was first re-dispersed in toluene and heated to 70 °C, then an appropriate amount of S : OLA solution was injected. The reaction was quenched by cold-water bath, and the absorption and PL spectra of the as-synthesized PbS QDs are shown in Fig. 4(e). The first-excitonic absorption peak position of the sample is around 785 nm, which is impressively consistent with that of two-step TBP route synthesized QDs. The corresponding PL peak is also around 890 nm. The high consistency of both absorption and PL peak wavelengths of QDs synthesized by the two-step TBP route and precipitated Pb(OH)Cl strongly suggests that Pb(OH)Cl is formed first during the two-step route and acts as Pb precursor for the synthesis of ultrasmall QDs. The PL FWHM (210 meV), however, is much broader for the QDs synthesized from precipitated Pb(OH)Cl. This can be ascribed to the involved washing process after the Pb(OH)Cl synthesis, which removed many OLA and TBP molecules in solution that can act as the ligands and control size uniformity during the QD synthesis process. Having that said, TEM image (Fig. 4(f)) of such obtained PbS QDs still shows relatively good dispersity without any obvious QD aggregation, indicating that Pb(OH)Cl is a very promising precursor for ultra-small PbS QDs synthesis.

The above investigations indicate that TBP can facilitate the formation of Pb(OH)Cl and lead to the formation of ultrasmall QDs in the two-step TBP route, although alkylphosphines were thought to only interact with S. The case was different from the one-step TBP route, where TBP–S and OLA–S were homogeneously mixed before their injection into the Pb precursor solution. As the nucleation is instantaneous, no Pb(OH)Cl formation is expected. In this case, the TBP mainly plays a role in retarding QD growth by strongly interacting with S and passivating surface S-sites (more information can be found in Mechanism investigations in ESI and Fig. S2†). As a result, ultrasmall QDs with single absorption and PL peaks could be obtained in the one-step TBP-route. So the actual roles of TBP in QD synthesis can be different depending on the way it is introduced. Based on these studies, the TBP route can be actually done in one-step or two-step injections for synthesizing ultrasmall QDs.

Moreover, the scale-up synthesis of PbS QDs by both one-step and two-step TBP routes has been performed (ESI†). The results show that both ultrasmall and slightly larger QDs in high quality can be synthesized at larger scale by the new TBP route, which strongly suggests that the TBP route, as a greener approach as compared to the TMS route, is a promising, facile way to produce large amounts of small sized PbS QDs.

LSC application

Significant overlapped absorption and PL spectra of QDs could induce serious reabsorption and thus lower the efficiency of LSCs, especially for large-area devices. In general, the performance can be improved by enhancing the PL QY of QDs and better separating their absorption and emission spectra. It has been reported that heterostructured UV-visible QDs, such as CdSe/CdS, can help to separate absorption and PL spectra and reduce re-absorption loss. In previous work, NIR PbS/CdS QDs have been confirmed to have a quasi-type II band alignment, in that, electron leakage takes place from the PbS core to CdS shell, causing the red-shift of PL spectrum and longer lifetime of electrons with respect to bare PbS QDs. This PbS/CdS core/shell structure was confirmed to efficiently reduce the reabsorption of LSC.

Herein, the two-step TBP route synthesized ultrasmall PbS QDs with the Stokes shift of ~0.25 eV were first coated by a thin CdS shell (~0.1 nm) via cation exchange method to increase the Stokes shift value to as large as ~0.36 eV and also to make the QDs more stable. These core/shell QDs exhibit a fairly high PL QY of 70%. They were then employed as a luminescent material in LSCs, which can absorb the light and re-emit photons in between 700 and 1100 nm, coupling very well with the optical excitation wavelength range of Si solar cells (absorbing up to ~1100 nm). As seen in Fig. 5(a), after transferring the core/shell QDs from solution into the polymer matrix followed by UV-initiated polymerization, the PL peak position and FWHM were not changed, indicating the excellent stability of synthesized PbS/CdS QDs as expected. The optical efficiency (ηopt) was measured with a definition of $\eta_{\text{opt}} = \frac{I_{\text{LSC}}}{I_{\text{sc}} \times G}$, where $I_{\text{LSC}}$ and $I_{\text{sc}}$ are the short circuit photocurrent from the Si diode coupled with a LSC and the short circuit photocurrent from the Si diode under direct illumination (AM 1.5G).

As seen in Fig. 5(b), the optical efficiency decreases with increasing length of the LSC devices mainly due to the reabsorption phenomena caused by the small overlap of the absorption and emission spectra of the QDs, where the G factor is defined as the top surface area divided by the area of side facing the solar cell (the other three sides were covered by mirrors while measuring the efficiency). The optical efficiency with the QD concentration of 24 μM is around 4% at G factor of 10, which is much higher than the previous record optical
efficiency (~1.4%) of the core/shell PbSe/PbS QDs based LSCs at a much higher QD concentration of 193 µM (G factor: 11) with a flat structure. Even at large G factor (G = 50, 10 cm in length) the ηopt is still around 1.2%, among the best efficiencies of the LSCs based on the CdSe/CdS QDs (1%), CdSe/Cd,PbS1−x QDs (1.15%), PbS/CdS QDs (1.1%) with similar G factors. It can be attributed to the high PL QY, large Stokes shift and good stability of TBP-route synthesized QDs; their integration into the polymer matrix does not lead to any dramatic degradation of their PL QY. Compared with previously reported giant core/shell QDs with a thick shell, a comparable Stokes shift was obtained for ultrasmall QDs with only a 0.1 nm thin shell. It is a significant way to overcome the trade-off between shell thickness and PL QY. In many cases, PL QY is inversely proportional to shell thickness, like the cases of CdSe/CdS and PbS/CdS. Moreover, higher temperature (over 200 °C) or longer reaction time (several hours or longer) for preparing the giant core/shell QDs can be avoided. For instance, we conveniently obtained PbS/CdS QDs (shell thickness: 0.1 nm) in 8 s at 100 °C. Overall, ultrasmall QDs synthesized by the TBP route are promising for LSC application in the NIR range by taking PL QY, separation of absorption/emission spectra and photo-stability of these QDs into consideration.

To further evaluate the performance of the LSC device based on PbS/CdS QDs, quantum efficiency (ηquan) defined as

\[ η_{quan} = \frac{I_{LSC}}{I_{Abs} \times G} \]

was calculated (Fig. 5(b)), where \( I_{Abs} \) is the short circuit photocurrent from the Si diode under the illumination of light absorbed by QDs. Similar to the trend of ηopt, the ηquan of the device decreases from 9.6% to 2.9% with increasing G-factor of LSCs from 10 to 50. The quantum efficiency gives an idea of the amount of photons that reach the edge of the LSC and so it is a useful indication of the feasibility to realize large-scale LSC. Also in this case, even at large G factor (G = 50), the internal quantum efficiency is still around 2.9%, one of the best...
values for NIR LSCs based on lead chalcogenides and also comparable to the values of the best LSCs involving other types of QDs such as CdSe/CdS. In addition, it can be further improved by increasing the shell thickness, resulting in more separated absorption and emission spectra, and thus less reabsorption in the LSC device. These results indicate that these ultrasmall QDs are quite promising for large-area LSC device application. LSC devices composed of relatively large PbS QDs and PbS/CdS QDs with a thick shell (0.5 nm) were also fabricated. Their device performance is shown in the ESL.

Fig. 5(c) shows that the as-prepared LSC device has quite good transparency, attributed to homogeneously dispersed PbS QDs in a polymer matrix. Moreover, a NIR camera with a 780 nm long-pass filter was used to capture the photograph of an illuminating LSC excited by a 636 nm laser light source (Fig. 5(d) and (e)). A large portion of the generated photons was successfully guided to the edge of the LSC device with brightness comparable to the excited area under direct illumination, indicating the good quality of the prepared LSC device.

Conclusions

In summary, the TBP route has been developed, for the first time, as an effective and less toxic way to synthesize high quality, ultrasmall PbS QDs, without involving the use of smelly S precursors (such as TMS) and a glove box. Via this method, PbS QDs with diameter below 2.5 nm can be synthesized, showing the optical absorption peak wavelength as short as 705 nm, which have been challenging to achieve with previously reported TMS-free methods. In addition to yielding quite high PL QY up to 90%, this synthesis route can be readily scaled up. By performing detailed investigation on experimental parameters and conducting structural, surface chemistry and optical characterization, the actual role of TBP in QD synthesis was found to be different depending on the way it was introduced into the synthesis. Surprisingly, it can promote the transformation of PbCl\textsubscript{2}–OLA to Pb(OH)\textsubscript{2}Cl, leading to the synthesis of ultrasmall PbS QDs. Moreover, it was confirmed that TBP is capable of slowing down the crystal growth process and passivating the surface S-sites. The high quality of such synthesized PbS QDs (and subsequently synthesized PbS/CdS QDs) was further demonstrated by the impressively high efficiency achieved by QD-based LSC devices, revealing the success of the developed TBP route and the high potential of these QDs in NIR optoelectronics.

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