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SUPPORTING INFORMATION

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

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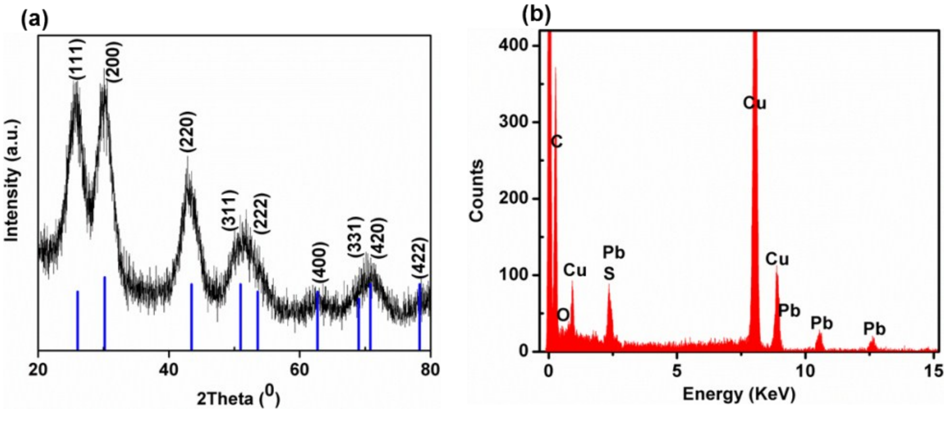
Table S1 Absorption and PL characteristics and calculated size of PbS QDs synthesized with different volumes of TBP.

Contents of TBP (μL)	**0**	**10**	**20**	**30**	**40**	**60**
Absorption Peak (nm)	1056	1028	951	876	705	N/A
Calculated QD Size (nm)	3.5	3.4	3.1	2.8	2.2	N/A
PL Peak (nm)	1136	1115	989	942	844	N/A
PL FWHM (meV)	119	100	107	122	197	N/A

N/A means that no QDs were collected.

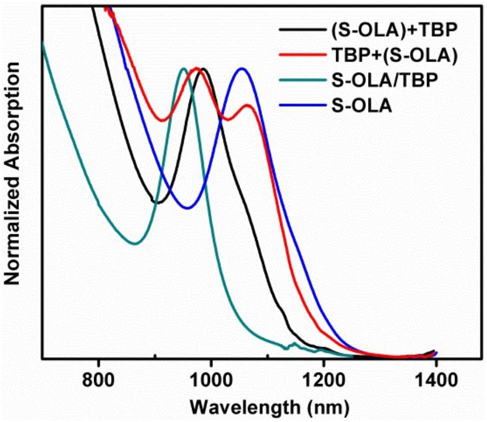
Figure S1. X-ray diffraction (XRD) spectrum (a) and energy-dispersive X-ray spectroscopy (EDS) of PbS quantum dots (QDs) with an average diameter around 3.1 nm. The XRD pattern is in accordance with the PbS standard JCPDS card no. 02-0699. EDS results confirm the QDs are composed of Pb and S.



Mechanism investigations. Understanding the effect of different molecular species on the formation of nanocrystals is crucial to control the diameter, dispersity, yields and properties of QDs and ultimately their utility in functional devices.[1] In this respect, it is important to know the role of TBP in synthesizing ultrasmall PbS QDs. For the normal $PbCl_2$-S synthesis, without the presence of any alkylphosphines, the mechanism investigations have been focused on the reactions between sulfur and amine.[1] It was reported that sulfur exists as S_8 rings at its standard state, which can firstly react with alkylamine to form the sulfur precursor alkylammonium polysulfides at relatively low temperature. Upon heating to a higher temperature, such as 130 ºC, the polysulfide ions react with excess amine to generate H_2S, which then react with lead precursors to form PbS QDs. For the TOP involved $PbCl_2$-S synthesis, it was reported that the presence of TOP can affect the "crystal growth" in a complicated way (for example, by forming S-TOP complex), but without really participating in the nucleation process.[2]

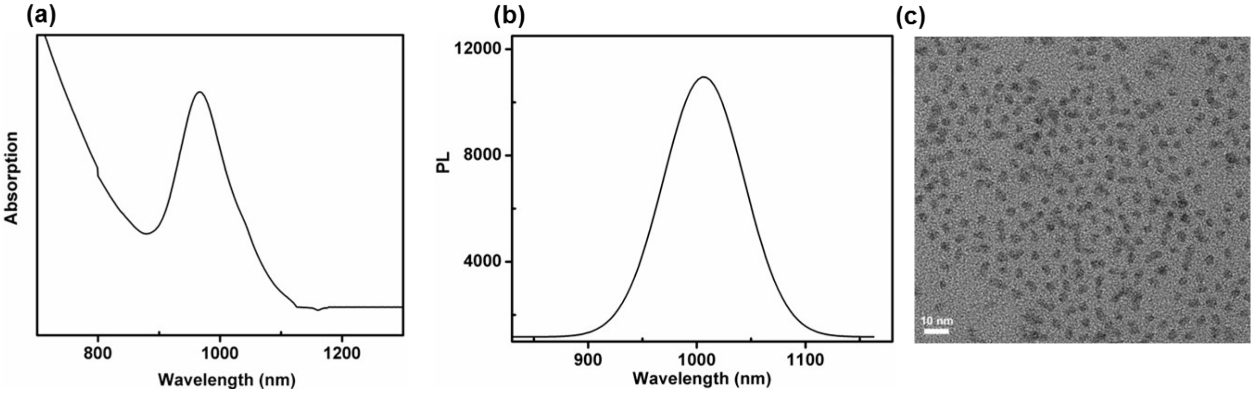
Herein, the effect of TBP on the nucleation and crystal growth of PbS QDs was investigated by varying the way TBP was introduced into the reaction solution (please note: in the one-step route mentioned in the manuscript, TBP was first mixed with the S-OLA solution and then one step injection of S-OLA/TBP was done). In one case, 20 µl of TBP was separately injected into the reaction solution immediately after the S-OLA solution being added to the pre-heated Pb precursor solution (denoted as (S-OLA)+TBP). The absorption spectrum of the obtained QDs with an absorption peak position around 985 nm is shown in Figure S2, which is clearly blue shifted as compared to the case of the TBP-free reaction. Assuming the nucleation process is instantaneous upon the S-OLA injection, this observation suggests that TBP affects QD growth by decreasing the chemical reactivity of the S precursor, highly likely due to the already known strong binding effect between phosphines and S although the TBP effect on the Pb precursor reactivity cannot be absolutely excluded either. In addition, the passivation of the surface S sites by TBP, as confirmed by ^{31}P NMR (Figure 3b), increases the barrier for the QDs growth. Both effects can decrease the growth rate of PbS QDs, leading to a smaller size and thereby an absorption peak at a shorter wavelength. Similar "retarding" effect on the crystal growth was also observed in our group by using TOP as an additive, although in that case we did not identify the presence of TOP on the QD surface.[3] Surprisingly when we switched the order of injections of S-OLA and TBP, bimodal absorption peaks were clearly observed, with one located at 973 nm close to that of QDs obtained by the one-step TBP route, and the other at 1065 nm close to that of the TBP-free sample. We speculate that TBP possibly has imposed certain effect on the lead precursor as well, which affects the nuclei formation, although usually we tend to think that alkylphosphines only interact with S. The effect of TBP (at larger amount) on the Pb precursor was investigated in depth in the manuscript, which was found to facilitate the formation of Pb(OH)Cl.

Figure S2. Two-step injection: absorption spectra of PbS QDs synthesized by injecting (S-OLA) and then 20 μL TBP (Black: (S-OLA)+TBP) and by injecting 20 μL TBP and then (S-OLA) (Red: TBP+(S-OLA)) into the Pb precursor solution; One-step injection: absorption spectra of PbS QDs synthesized by injecting the mixture of S-OLA and TBP (TBP: 20 μL, dark green: S-OLA/TBP), and by injecting S-OLA only (no TBP, Blue: S-OLA) into the lead precursor solution.



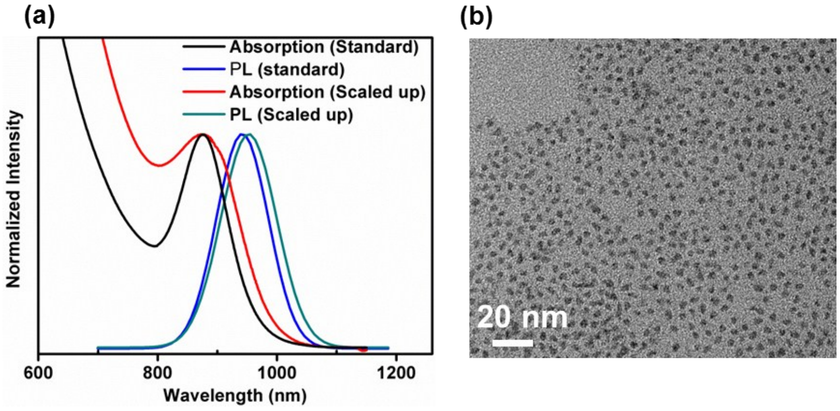
Synthesis scale-up of ~3.1 nm PbS QDs. The quantities of major chemicals were enlarged by 6-folds ($PbCl_2$:12g S:120 mg TBP: 120 μl), whereas the volume of OLA for dissolving $PbCl_2$ and S was slightly increased (50 ml) and unchanged (5 ml), respectively. The absorption spectroscopy, photoluminescence (PL) spectroscopy and TEM were employed to determine the quality of the synthesized QDs. The absorption spectral with well-shaped narrow peak around 967 nm has been obtained for the as-prepared PbS QDS as shown in Figure S3(a), and its corresponding PL spectrum with strong intensity and low value of full width at half maximum (FWHM) (98.6 meV) is shown in the Figure S3(b). Figure S3(c) further proves that the as-prepared QDs have uniform size distribution, which accords well with the PL and absorption results. We conclude that the high quality PbS QDs have been successfully obtained by the up-scaling reaction. Each batch yields around 470 mg of QDs. There is still large room for further quantity increase.

Figure S3. Characterizations of PbS QDs (~3.1 nm in diameter) synthesized by one-step TBP-route in the scaled-up reaction: absorption spectrum (a), PL spectrum (b), and transmission electron microscopy (TEM) image (c).



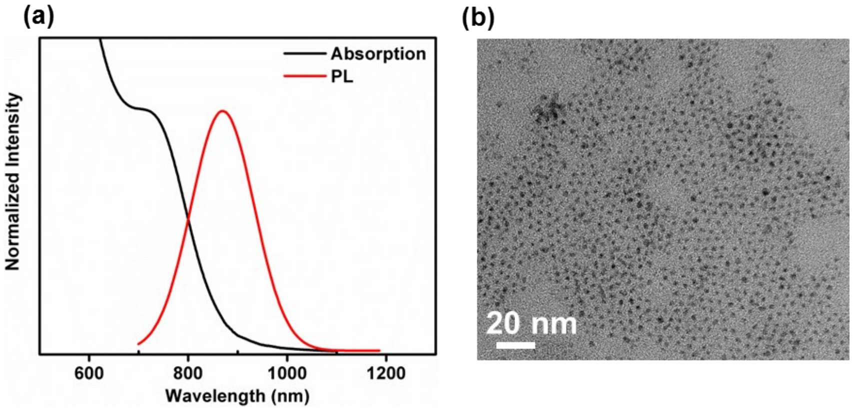
Synthesis scale-up of ~2.8 nm PbS QDs. In this synthesis, the quantities of major chemicals were enlarged by 5-folds ($PbCl_2$: 10 g; S: 100 mg), whereas the volume of OLA for dissolving $PbCl_2$ and S was slightly increased (50 ml) and unchanged (5 ml), respectively. The volume of TBP was increased by 10 folds. Absorption spectroscopy, PL spectroscopy and TEM were employed to assess the quality of the QDs synthesized at the larger reaction scale. Both absorption and PL peaks remain at similar wavelengths after reaction scale-up (Figure S4(a)). Although the absorption peak is broadened, the FWHM of the PL peak remains almost unchanged. The integrated PL intensity of the up-scaled sample is around 89% of that of the standard sample, before scaling up, measured at the same QD concentration. Fig. S4(b) confirms that the as-prepared QDs have uniform morphology and size distribution with the average diameter around 2.8 nm, consistent with the results got from the PL and absorption spectra. Clearly high quality PbS QDs can be obtained by the up-scaled reaction, which yields QDs around 150 mg.

Figure S4 Characterizations of PbS QDs synthesized by the TBP-route in scale-up reactions: (a) absorption and PL spectra and (b) TEM image of QDs (~ 150 mg per batch) synthesized by scaling up the synthesis for 3.1 nm QDs (one-step injection). Absorption and PL spectra of PbS QDs with similar diameter synthesized in a standard scale are also included for comparison.



Synthesis scale-up of PbS QDs with diameter ~2.3 nm. Synthesis of PbS QDs with first-excitonic absorption peaks shorter than 800 nm was also successfully scaled up by separately injecting large amounts of TBP firstly, and then S-OLA (TBP:$PbCl_2$:S = 1:1:0.42 in molar), instead of using the one-step TBP-route. As an example, PbS QDs with an absorption peak at ~730 nm and a PL peak at 870 nm can be synthesized from one batch at the quantity of ~200 mg (Figure S5).

Figure S5 Absorption/PL spectra (a) and TEM image (b) of ultra-small PbS QDs synthesized by the two-step injection.



Synthesis of PbS/CdS QDs with the shell thickness around 0.5 nm. PbS QD suspension in toluene (1 mL, Absorbance = 3 at the first exciton peak) was first diluted to 10 mL. After N_2 bubbling for 30 min, the PbS QD suspension was heated to 100 °C, followed by the immediate injection of 1 ml of Cd-oleate solution. The reaction was then allowed to proceed for different time in order to get different shell thickness. Specifically, for growing the CdS shell of 0.5 nm in thickness for the LSC device fabrication, the reaction was stopped after 5 h. Finally, the PbS/CdS QDs were purified and re-dispersed in toluene for LSC device fabrication. TEM image and energy-dispersive spectroscopy (EDS) of obtained PbS/CdS are shown in Figure S6.

Figure S6. TEM image (a) and EDS spectrum (b) of PbS/CdS QDs synthesized via cation exchange for luminescence solar concentrator (LSC) application.

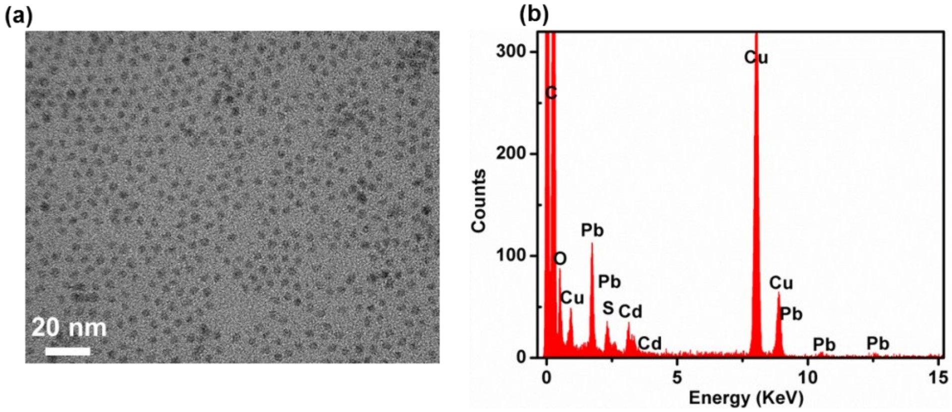


Figure S7. (a) Absorption and PL spectra of PbS QDs (first excitonic peak: ~900 nm; PL: ~960 nm) in solution and a polymer matrix. (b) Optical/quantum efficiency of PbS QDs embedded LSCs with different G factors. (c) Absorption and PL spectra of PbS/CdS QDs (Shell thickness: ~0.5

nm) in solution and a polymer matrix. (d) Quantum efficiency of PbS/CdS QDs embedded LSC devices with different G factors.

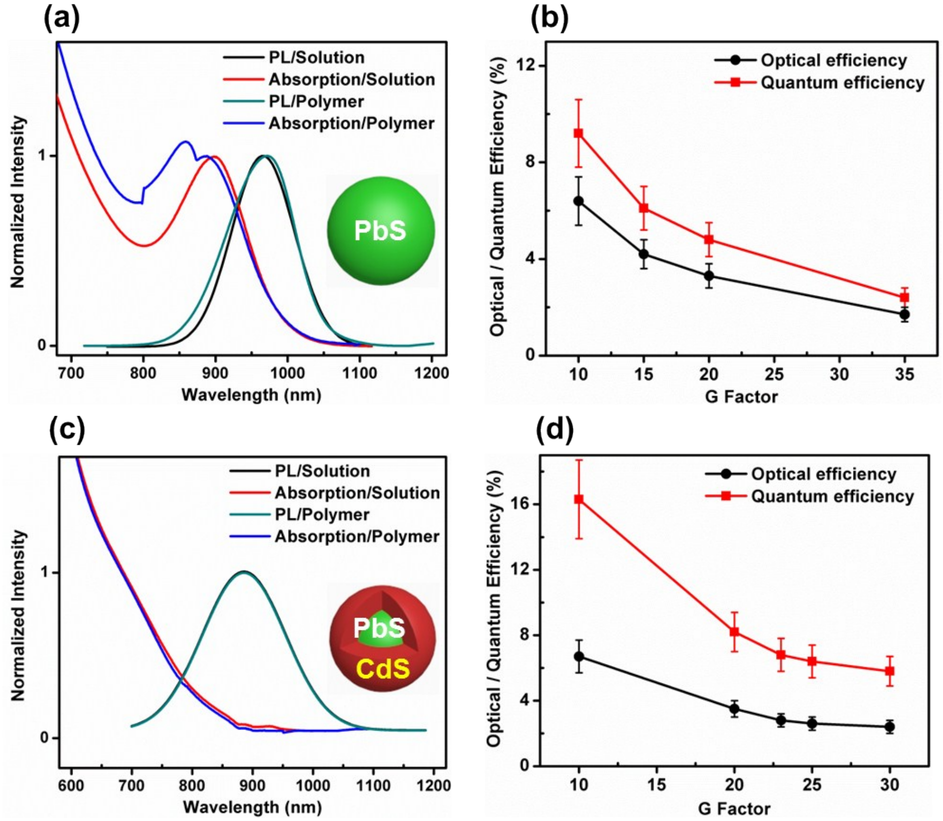


Table S2 Detailed information for fabricated LSC devices using relatively larger PbS (first excitonic peak: ~900 nm; PL peak: ~960 nm) and thicker-shell (0.5 nm) PbS/CdS QDs as luminescent materials, respectively.

Samples	Concentration of QDs (μM)	Length (cm)	G factor	Optical efficiency (%)	Quantum efficiency (%)
PbS-1	14	2	10	6.4	9.2
PbS-2	14	3	15	4.2	6.1
PbS-3	14	4	20	3.3	4.8
PbS-4	14	7	35	1.7	2.4
PbS/CdS-1	24	2	10	6.72	16.3
PbS/CdS-2	24	4.6	23	2.81	6.8
PbS/CdS-3	24	5	25	2.63	6.4
PbS/CdS-4	24	5.8	29	2.38	5.8

Error of quantum/optical efficiency: ±10%.

Determination of PbS QD quantity in the scaled-up reaction

Firstly, we determined the molar concentration of synthesized PbS QDs in toluene using the Beer-Lambert's law: $A = \varepsilon CL$, where A is the absorbance at the position of the first exciton absorption peak for a given sample, ε is the extinction coefficient per mole of PbS QDs, C is the molar concentration of QDs, and L is the light path length depending on the cuvette. ε was determined using $\varepsilon = 19600\ r^{2.32}$,[4] where r is the radius of QDs. R can be calculated by the following formula: $E = 0.41 + 1/(0.0252d^2 + 0.283d)$, where E and d are the bandgap and diameter of obtained QDs, respectively.[5] Then, the calculated C was converted to mass concentration.[2] Finally, the product yield per batch can be obtained by using the mass concentration multiplying the total volume of QDs solution.

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