

Red Green Blue Emissive Lead Sulfide Quantum Dots: Heterogeneous Synthesis and Applications

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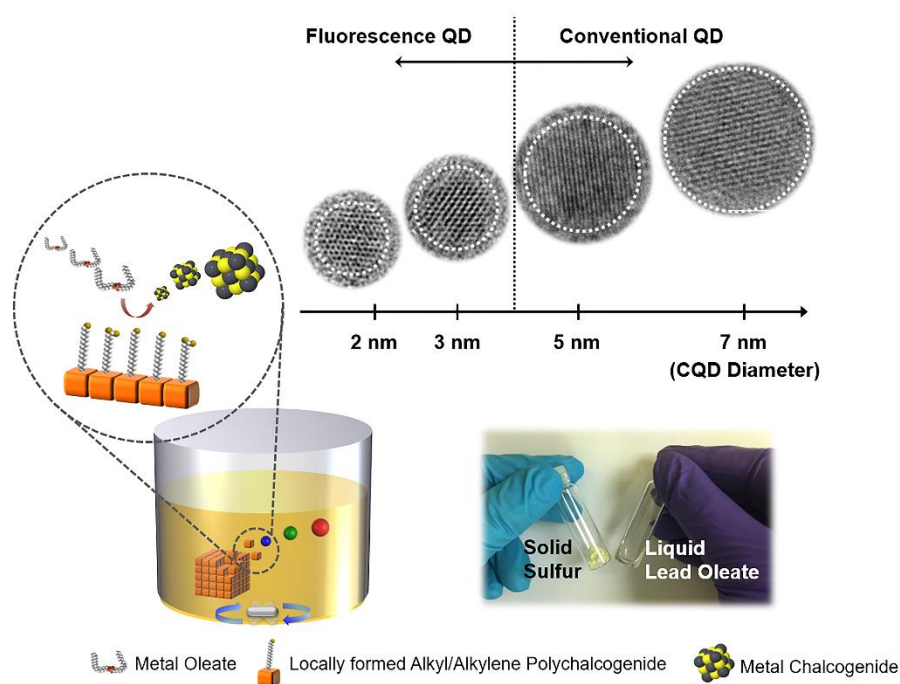
Abstract

Visible emission colloidal quantum dots (QDs) have shown promise in optical and optoelectronic applications. To date, these QDs are typically comprised of relatively expensive elements in the form of indium, cadmium, and gallium since alternative candidate materials exhibiting similar properties have yet to be realized. Herein, for the first time, we report red, green, blue (RGB) photoluminescences with quantum yields of 18 % from earth-abundant lead sulfide (PbS) QDs. The visible emissive property is mainly attributed to a high degree of crystallinity even for the extremely small QD sizes (1 - 3 nm), which is realized by employing a heterogeneous reaction methodology at high growth temperatures (> 170 °C). We demonstrate that the proposed heterogeneous synthetic method can be extended to the synthesis of other metal chalcogenide QDs, such as zinc sulfide and zinc selenide, which are promising for future industrial applications. More importantly, benefiting from the enlarged band gaps, the as-prepared PbS solar cells show an impressive open circuit voltage (~ 0.8 V) beyond that reported in the literature.

Introduction

Colloidal Quantum Dots (QDs) have attracted considerable attentions from the scientific communities due to their outstanding photophysical properties.^[1-5] Currently, the need for visible emission QDs has increased dramatically, mainly due to their deployments in commercial applications such as image sensors, solar cells (QDSCs) and displays.^[5-7] However, at present, RGB-emissions can only be realized from expensive cadmium, indium or gallium QDs which impede their long-term sustainability.^[5] Earth-abundant lead sulfide (PbS) QDs are generally considered as promising materials for QDSCs.^[2, 4, 5] Recently, there has been a high demand for producing wider band gap PbS QD to increase the photovoltage of the cell and compensate for the troublesome open circuit voltage (V_{oc}) deficiency.^[8-11] Theoretically, by decreasing the size of the QD, the band gap of PbS can be expanded from 0.4 eV to more than 3 eV.^[12-14] However, due to the limitations of the fabrication techniques, PbS QDs are still absent from visible light emissions.^[5, 6] ‘Hot-Injection’ is undoubtedly the best method for producing high-quality QDs that has been reported to date.^[6, 15] The merits of this approach are the ability to combine ‘nucleation’ and ‘growth’, which generates QDs with a high degree of crystallinity and narrow size distributions.^[15, 16] Commonly used organochalcogen compounds are activated by coordination to Lewis acidic metal centers, or spontaneously generating vigorous hydrogen chalcogen (i.e. thiols, chalcogen radicals, or H_2S) species, which are highly reactive to metal precursors.^[15, 16] Indeed, the PbS reaction equilibrium constant (e.g. $Pb^{2+} + H_2S$) can be reached up to 3×10^6 M in literature.^[17] While these intense reactions are beneficial for fast nucleation and growth through the ‘hot-injection’ process,^[16] they are prohibitive in terms of producing extremely small size PbS QDs and thus band gaps above 1.6 eV.^[5, 17-19]

Herein, by controlling the reactivity of precursors, we have successfully synthesized emissive PbS QDs that cover the whole visible wavelength. We highlight the generality of this method by applying it to other materials. Furthermore, by employing as-prepared wide band gap PbS QDs, we demonstrate an outstanding open circuit voltage (V_{oc}) improvement from p-n junction QDSCs.



Scheme 1. An illustration of as-proposed heterogeneous synthesis approach for metal chalcogenide QDs. The photograph highlights the physical nature of the solid state S and the liquid state lead oleate. The inset HRTEM images are PbS QDs which demonstrate the size controllability of the proposed methods.

Results and Discussion

The chance to make the reaction outcomes to achieve such wide band gap domains would have to interrupt the nanoparticle growth.^[11, 18] The primary idea underlying the synthesis of the wide band gap PbS QDs is to control the kinetic reaction activity of the precursors.^[20] i) The oleic acid (OA) concentration is limited to a quantity barely sufficient to achieve particle stabilization (e.g. OA:Pb:S = 4:2:1).^[4, 18] Under these conditions, the monomer reactivity increases and the nucleation provides a very large number of small PbS nuclei that grow slowly.^[4, 18] ii) Because alkyl or alkylene polysulfides which are generated from the solubilization of sulphur (S) in the octadecene (ODE) have been demonstrated to have much lower activities toward metal counterparts.^[21-24] Instead of the commonly used liquid organochalcogen compounds,^[20] solid state (S) is employed as the S source and lead oleate dispersed ODE is employed as the Pb source. iii) Unlike ‘hot-injection’ or hydrothermal approaches that have been used to produce small-sized QDs or magic-sized clusters at low temperatures^[11, 21, 25-29] (a detailed comparison is listed in Table S1 at supporting information SI), we employ a high reaction temperature (> 170 °C) through using

sparingly soluble solid S flakes as precursor to achieve these emissive PbS QDs. A high-temperature reaction is beneficial for producing QDs with a high crystal quality,^[15, 29] and thus realizing visible photoluminescence (PL). Fourier transforms infrared spectroscopy reveals that a depletion of the olefin moieties proceeding concomitantly with the elevation of reaction temperature, which indicates the on-site formation of the alkyl or alkylene polysulfide (SII, Figure S1 and scheme S1). Due to the sulfur bond enthalpy that enables bond-breaking above 150 °C,^[23, 24] no detectable reaction appeared to take place below 150 °C, and visible emission PbS QDs can only be formed when the reaction occurs above 170 °C. As illustrated in Scheme 1, by using this liquid and solid heterogeneous reaction methodology, we have successfully controlled the reaction between the metal and the chalcogen precursors at high temperatures, which enable the synthesis of extremely small size PbS QDs with a high degree of crystallinity (SI and Table S1).

PbS QDs possess a large bulk exciton Bohr radius (20 nm),^[14] which can create an extremely strong quantum confinement that allows us to tune its band gap across the entire visible spectrum.^[11] Figure 1a (inset image) displays the as-prepared PbS QDs in different sizes, which are dispersed in toluene with blue to red emission under UV irradiation ($\lambda = 365$ nm). As anticipated in previous theoretical-based studies, the band gap increased and ultimately converged to the first allowed excited state ($X \rightarrow A$) of the PbS molecule when the particle size decreases. The band gap approaches the value of the first allowed excited state (above 2 eV) at around 2 nm.^[13, 14] The sizes of as-prepared QDs are determined from transmission electron microscopy (TEM) measurement and also calculated from X-ray diffraction pattern based on Scherrer equation (SIII, Table S2). As rationalized in Figure 1a, our experimental values (size/band gap) are distributed around the first allowed excited state, which agrees well with previously theoretical and experimental results.^[12-14, 30, 31] Figure 1b-e shows TEM images of as-prepared QDs which exhibit quasi-spherical appearances. The diameter of these QDs is 1.9 ± 0.3 nm (blue), 2.5 ± 0.5 nm (yellow), 2.7 ± 0.4 nm (red) and 3.1 ± 0.1 nm (dark red) respectively. The size distributions of the fluorescent PbS QDs are determined from TEM size statistical analysis and it is found that deviations in size are less than 0.4 nm. The high crystallinity of these fluorescent PbS QDs is demonstrated by using various experimental techniques. Through high resolution TEM analysis (HRTEM, Figure 1c-f), the clearly resolved lattice fringes of the {111}, {220}, {200} planes can be indexed which are close to the PbS bulk crystal values (PDF = 78-1057, $d_{111} = 3.4 \text{ \AA}$, $d_{220} = 2.1 \text{ \AA}$, $d_{200} = 3.0 \text{ \AA}$). High-resolution synchrotron XRD (SIII, Figure S2), selected-area electron

diffraction (SAED) and additional high-resolution TEM images (SIII, Figure S3) further confirm the PbS rock-salt characteristics. Moreover, a uniform lead-rich stoichiometry is revealed from the quantized X-ray photoelectron spectroscopy analysis (SIV, Figure S4, Table S3), which is consistent with the lead-rich nature for small sized PbS QDs.^[30, 31]

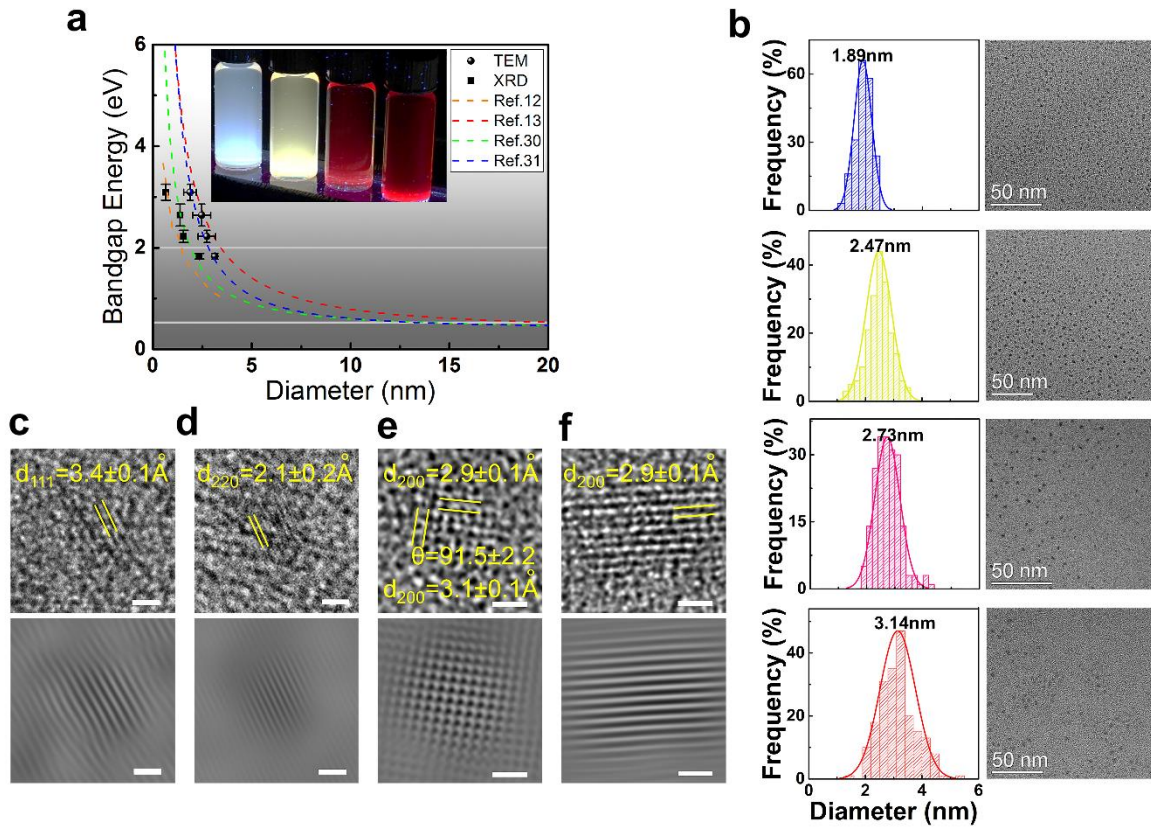


Figure 1. a) The dashed lines represent the dependence of the band gap on the sizes of the PbS QDs that were calculated from the tight-binding model,^[12] hyperbolic band model,^[13] and experimental empirical models.^[30, 31] (●) and (■) represent current experimental data obtained from TEM and XRD analysis, error bars are generated from the standard deviations obtained from the analysis. Horizontal lines highlight the 2 eV and 0.4 eV band gap energies. Inset image shows the PbS QDs dispersed in toluene under UV illumination ($\lambda = 365$ nm). b) TEM images and the size distribution histogram analysis results for each QDs. HRTEM images of the blue, yellow, red and dark red PL QD are shown in c, d, e and f respectively. Scale bars are 1 nm for the HRTEM image (top) and the inverse fast Fourier transform enhanced images (bottom).

The optical band gaps extracted from the fabricated PbS QDs are determined from absorption spectroscopy as presented in Figure 2a (Table S1). These plots show that the absorption edge of the QDs can cover from the border of the ultraviolet (UV) to the near infrared (NIR) of the spectrum. In Figure 2b, due to the good crystallinities and highly confined regimes, the ultra-small sized QDs show visible PL emission peaks compared to

previous works (Table S1).^[4, 18-20, 25, 30, 31] A comparison between the full width at half maximum (FWHM) values extracted from the PL spectra and TEM size distribution was performed (SV, Figure S5). The data suggests that the relatively broad PL peaks and Stokes shifts (inset of Figure 2b) are attributed to the small exciton binding energies rather than the poly-dispersed size distribution.^[13, 14] The quantum yields (Φ_{QY}) of PbS QDs fabricated through conventional ‘hot-injection’ approaches are reported ranging from 5% to 70%.^[32] However, the optical band gaps of these QDs mainly cover NIR range (800-2000nm).^[3, 32] The prominent measurable PL emission enables us to quantify the visible emission properties through a quantum yield (Φ_{QY}) analysis.^[3, 33] By using Rhodamine B (in absolute ethanol) as a standard reference, the Φ_{QY} of the PbS QDs is found to be as large as 18 % (SV, Figure S6, Table S4).

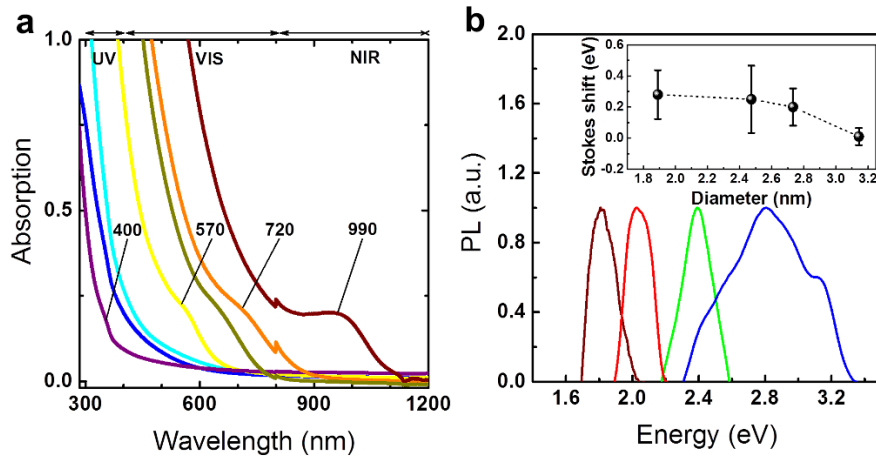


Figure 2. a) Absorption spectra of the PbS QDs. b) PL spectra of four different sized PbS QDs emitting at different wavelengths. Inset: a plot of the Stokes shift as a function of the size of the QD. The error bars are generated from various absorption onset values.

The remarkably large band gap can also be demonstrated by incorporating these QDs into current *p-n* junction QDSCs where they exhibit large improvements in the open circuit voltage (V_{oc} , see detail in SI and SVI). Onsets of external quantum efficiency (EQE) curves are generally considered as references when comparing the measured V_{oc} to the Shockley-Queisser limit.^[9] In the present work, EQE spectra and J-V curves are obtained under AM 1.5 G (ASTM-G173-03) with solar cell mask area of 0.012 cm². Indeed, by applying the as-prepared PbS QDs in QDSCs, the EQE onset (Figure 3a) can be enhanced to 1.61 eV which generates 0.8V V_{oc} as measured from J-V curves (Figure 3b). Figure 3b exhibits six representative J-V curves from as-prepared PbS QDSCs. Accompanied by the changing of

band gap from 0.84 eV to 2.22 eV, perceptible increments of V_{oc} can be resolved from the intersections at the abscissa axis. (Full range EQE spectra can be found in SVII, Figure S9) Ultraviolet photoelectron spectroscopy indicates that the enlarged band gaps increase the band offset between operation junctions, which contribute to the V_{oc} improvement (SVI, Figure S7 and Figure S8). For instance, 1.83 eV PbS QDSC exhibits a 0.71 V open circuit voltage with 4.6 % efficiency, which is beyond previous reports under similar operation junction.^[1, 8] To ensure the validation of the measurement, a comparison of current densities extracted from J-V curve and EQE spectrum integration is supplied. The J_{sc} value which is calculated by integrating the EQE spectra (14.97 mA/cm^2) under the AM1.5G solar irradiation shows a good agreement with the measured J_{sc} (14.89 mA/cm^2 , more details can be found in Figure S10). Comparisons between the as-measured V_{oc} to the theoretical limits^[8, 34] and other QD solar cells^[8, 35-40] are summarized in Figure 4 and Table S5. Benefiting from the enlarged band gaps, the as-prepared PbS QDSCs demonstrate outstanding V_{oc} improvement compared to previous works. In spite of the promising performance in our QDSCs, there are still many parameters such as current density and fill factor need to be optimized before catching up the world-leading efficiency devices. Take 1.83 eV PbS QDSC as an example, our current density is much smaller than the theoretical limit, which suggests that there is a substantial potential for future developments on the wide band gap PbS in QDSCs. Specifically, we believe that optimizations of the QD ligand engineering or operation junction such as applying them into cascaded or tandem QDSCs can improve the current density and fill factor, which can lead to further improvements in QDSC efficiency.^[4, 8, 10, 11, 41]

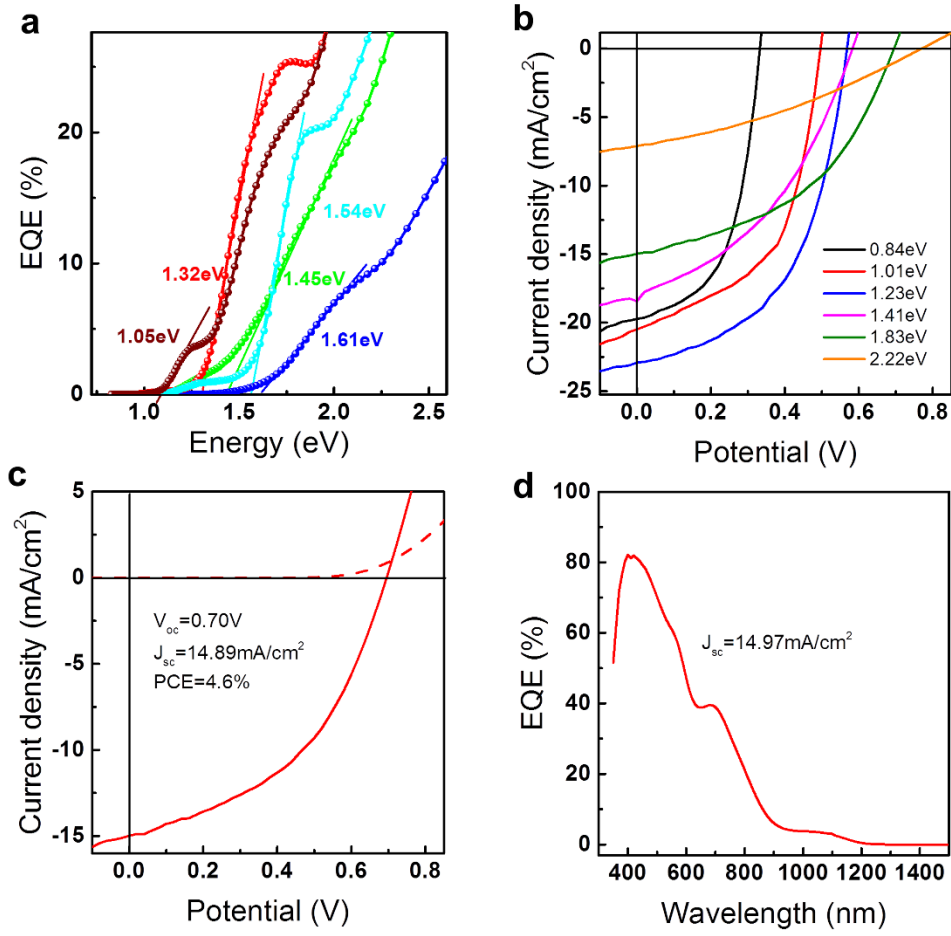


Figure 3. a) The EQE onsets extracted from as-prepared PbS QDSCs. b) Represented J-V curves of the QDSC with PbS QDs band gap from 0.84 eV to 2.22 eV under AM1.5G illumination. c) and d) Typical J-V curves and EQE spectra from 1.83 eV PbS QDSCs. V_{oc} , PCE and J_{sc} values for these cells (9 samples) are equal to $0.71 \pm 0.01V$, $4.61 \pm 0.1\%$ and $14.9 \pm 0.2 \text{ mA/cm}^2$, respectively.

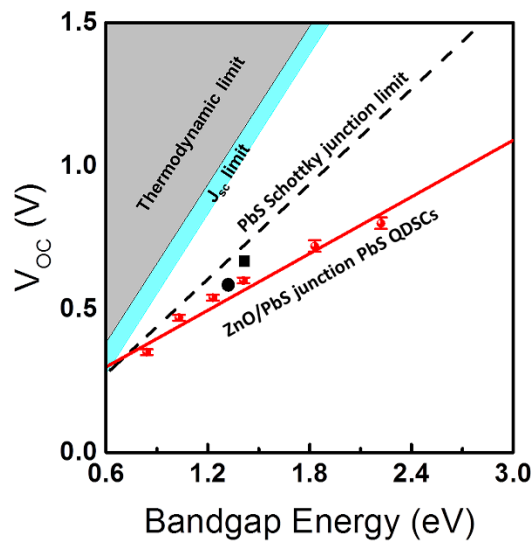


Figure 4. The limits of the V_{oc} as a function of PbS QD band gaps [8, 34]: the thermodynamic limit (grey), the J_{sc} limit (cyan), previously reported Schottky junction limit (black dash line), and a linear fit (red solid line) of

measured V_{oc} values (red symbols) from as-prepared PbS QDSCs which shows the possible V_{oc} limit trend for the p-n junction solar cell. (■) and (●) represent current world-leading PbS QDSCs which are operated under Schottky junction ($V_{oc} = 0.69$ V, PCE = 1.4 %) and p-n junction ($V_{oc} = 0.61$ V, PCE = 11.28 %) respectively.^[8, 35]

The applicability and the reproducibility of the proposed method are confirmed by fabricating Zn-based chalcogenide QDs. Owing to the heterogeneous reactivity control, Zn and chalcogenide precursors react slowly at an elevated temperature which results in high luminescent blue emission ZnSe QDs (PL peaking at 425 nm, Figure 5a) and ZnS QDs (PL peaking at 415 nm, Figure 5b) with a good crystallinity (Materials and Method in SI). TEM analysis determines the size of the as-prepared ZnSe and ZnS to be 2.22 ± 0.4 nm (Figure 5c) and 3.01 ± 0.46 nm (Figure 5d), respectively. The Zinc Blende ZnSe and Wurtzite ZnS crystal structures are also identified through SAED analysis (see detail in SVIII and Table S6).^[22, 42, 43] In the right panel of Figure 5c, two main reflections of 111, 200 can be indexed. The lattice constant, a , calculated from the average of each reflections is 5.55 ± 0.1 Å, which is consistent with its bulk value (5.618 Å, PDF = 80-0021). In the right panel of Figure 5d, The 102 reflection is identified which affirms its hexagonal nature of as-prepared ZnS QDs.^[44] The lattice constants calculated from the average of each reflection are $a = 3.60 \pm 0.1$ Å and $c = 6.24 \pm 0.1$ Å which are close to the bulk values ($a = 3.77$ Å, $c = 6.188$ Å, PDF = 80-0007). These promise and highly luminescent blue QDs demonstrate the potential for industrial applications and also motivates further studies on heterogeneous nanoparticles synthesis.^[5, 22]

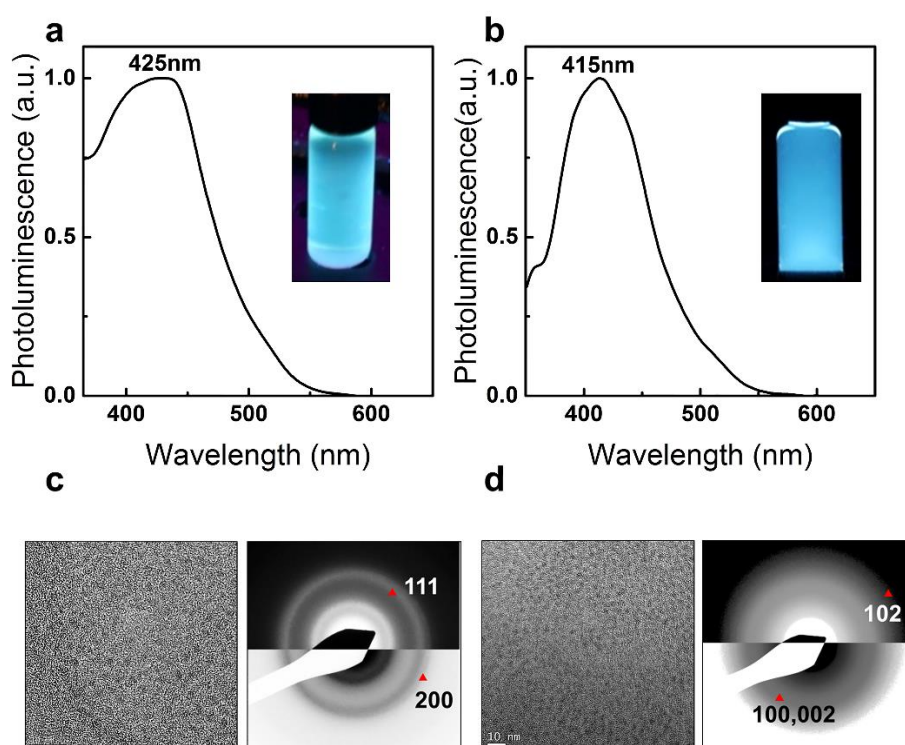


Figure 5. PL spectra of a) ZnSe QDs and b) ZnS QDs. Inset images show the PL from QDs dispersions in toluene under UV illumination ($\lambda = 365$ nm). c) A TEM image (left) and SAED pattern (right) of ZnSe QDs with a scale bar of 10 nm. d) A TEM image (left) and SAED pattern (right) of ZnS QDs with a scale bar of 20 nm.

Conclusion

In summary, for the first time, earth-abundant RGB emission PbS QDs have been synthesized by using a liquid and solid heterogeneous reaction methodology. We demonstrate the generality of this synthetic method by effectively producing other metal chalcogenide QDs with visible PL emission. By deploying fluorescence PbS QDs into QDSCs, prominent V_{oc} improvements (0.8 V) have been achieved. These findings eventually bring PbS QDs into the visible emission QD family and also set a new V_{oc} record for PbS QDSCs. It should encourage future works on their use in solar cell technologies as well as the enhancement of Φ_{QY} for light emitting applications.

Experimental Section

Synthesis and purification of visible emissive PbS QDs: 2.106 mmol PbO, 4.212 mmol oleic acid and 20 mL of ODE were loaded in a two neck flask. The solution was degassed at 100 °C in vacuum for two hours. Subsequently, 1 mmol sulfur flake was slowly added to the solution at room temperature under Ar. Different sizes of fluorescence PbS QDs were formed at elevated temperature (above 170 °C). QDs were purified by ethanol and recovered by hexane through a centrifugation process. The QDs were finally dispersed in toluene with a weight concentration of 50 mg/mL for device fabrication and characterization. Detail description can be found in the ref. ^[45] and supporting information.

Solar cells fabrication and characterization: Acetone, ethanol, and 2-isopropanol were used for the cleaning of patterned ITO. The ITO substrates were treated with oxygen plasma for 5 minutes before device fabrication. ZnO layers were formed by spin coating a solution of ZnO nanoparticles (50 mg/mL) onto ITO substrates at 2000 rpm for 30 seconds. Then the ZnO films were annealed at 250 °C for 10 minutes on a hot plate. QD solution (50 mg/mL) was spin casting onto the ZnO layer at 2000 rpm for 15 seconds. A tetrabutylammonium iodide (TBAI) solution (10 mg/mL in methanol) was then applied to the substrate for 30 seconds and then spun at 2000 rpm for 30 seconds, followed by two rinse-spin steps (30 seconds for each step) with methanol. For the 1,2-ethanedithiol (EDT) layers,

an EDT solution (0.02 % volume in acetonitrile) was applied to the substrate with a spin casting fashion, following by two times of acetonitrile washing. Au contact was thermally evaporated onto the films through shadow masks by EDWARD thermal evaporator. The device areas were defined by applying pre-defined masks (0.012 cm^2). J-V curves were recorded using a Keithley 2400 under simulated AM1.5 solar light illumination by a LOT Quantum Design simulator (LSE340/1/850.27C) for power conversion efficiency (PCE) calculation. The light intensity was calibrated with a RERA SOLUTIONS silicon reference cell (RQS4695) before each measurement. External quantum efficiency (EQE) measurement is performed by employing a SpeQuest QE system. The QE system has a 100 W Quartz Tungsten Halogen light as the photon source, equipped with a 150 mm F/4.2 monochromator, a SR830 DSP Lock-In Amplifier (locked to light chopped at 83 Hz) and a Melles Griot IV converter. The wavelength range is from 350 nm to 1800 nm and all the measurement are calibrated by a NIST traceable Silicon (200 nm - 1100 nm) reference cell and NIST traceable Germanium (700 - 1800 nm) with area pre-defined mask (0.012 cm^2).

Author Contribution

B. Hou and S. Cha carried out experiment design, experiment and data analyses. Y. Cho, B. Kim, Y. Lee, and J. Hong carried out QDSC fabrication and characterisation. D. Ahn, S. Lee, J. Park and J. Sohn carried out structural and optical analysis. H. Im, S. Morris, J. Sohn and J. Kim contributed to scientific discussion and provided experimental guidance. B. Hou and S. Cha wrote the manuscript and all authors reviewed the manuscript.

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