Supporting Information

Evolution of Long Range Bandgap Tunable Lead Sulfide Nanocrystals with Photovoltaic Properties

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Materials: Lead nitrate ([Pb(NO$_3$)$_2$], Aldrich, 99%), thiourea ([SC(NH$_2$)$_2$], Aldrich ≥ 99%), trioctylphosphineoxide (TOPO, Aldrich, 90%) and hexadecylamine (HDA, Aldrich, 90%) were used as received condition. Anhydrous methanol, chloroform, isopropanol, toluene and acetonitrile were used as solvent for purification, dispersion and device fabrication. Indium tin oxide (ITO) coated glass slide (15-25 Ω/sq, Aldrich) and Aluminium wire [Al, Aldrich, 99.999%] were used for electrode preparation.

PbS nanocrystal synthesis: For the synthesis of 5.5 nm PbS nanocrystal, 0.166 g lead nitrate and 0.035 g thiourea were added into 2 g TOPO and allowed to react for 10 min at 110°C with continuous stirring under nitrogen flow. Note that the use of anhydrous TOPO will result in
improved nanocrystals size distribution whereas old and water absorbed or air exposed TOPO will give aggregated large sized peanut like nanostructures. The temperature was then increased to 150°C, where the reaction mixture turned into milky color. At this condition, 0.4 g transparent melted HDA was injected to the first reaction flask in one shot. The color of the reaction mixture turned to deep reddish black instantaneously, where annealing was carried out for another 30 min. For bandgap controlling, before injection of the molten HDA, the reaction solution temperature was adjusted according to the desired nanocrystal bandgap (see Table S1). When the temperature stabilized, 0.4 g melted HDA was rapidly injected into the hot solution. We controlled the nanocrystal bandgap and monodispersity by adjusting the injection temperature of HDA (110°C-160°C) and the growth time of the nanocrystals (2 min to 60 min). Once complete, the reaction was rapidly cooled to 70°C by water bath and subsequently quenched by injecting 8 mL of methanol. The nanocrystals were purified by precipitation twice in methanol by centrifugation at 5000 rpm for 5 min and once in chloroform/methanol mixture and stored by dispersing in chloroform or toluene.

The proposed reaction pathway for the formation of our PbS nanocrystals is

\[
\begin{align*}
\text{TOPO} \rightarrow R_3P=O \quad [R = \text{octyl group}], \quad \text{CS(NH}_2\text{)}_2 \rightarrow S=C(\text{NH}_2)_2 \\
\text{Pb(NO}_3\text{)}_2 \rightarrow \text{Pb}^{2+} + 2 \text{NO}_3^- \\
R_3P=O \text{ heated to } 110^\circ\text{C} \quad \rightarrow \quad \text{R}_3\text{P}=\text{O}^{5+}\text{Pb}^{2+} \quad \rightarrow \quad \text{PbS NCs} + \text{CO(NH}_2\text{)}_2 + \text{NO}_2
\end{align*}
\]

(Lewis adduct) (Whitish complex) (Capped with TOPO & HDA)
Table S1. Experimental conditions, resultant sizes, absorbance and bandgap energies of different PbS nanocrystals are presented.

<table>
<thead>
<tr>
<th>Samples</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection temperature (°C)</td>
<td>110</td>
<td>120</td>
<td>130</td>
<td>150</td>
<td>160</td>
</tr>
<tr>
<td>Growth time (minutes)</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Size (nm)</td>
<td>2.3 ± 0.2</td>
<td>2.7 ± 0.2</td>
<td>3.5 ± 0.3</td>
<td>5.5 ± 0.5</td>
<td>10 ± 0.5</td>
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<tr>
<td>Absorbance wavelength (nm)</td>
<td>730</td>
<td>838</td>
<td>1040</td>
<td>1270</td>
<td>2050</td>
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<tr>
<td>Bandgap energy (eV)</td>
<td>~1.7</td>
<td>~1.5</td>
<td>~1.2</td>
<td>~1.0</td>
<td>~0.6</td>
</tr>
</tbody>
</table>

**Characterization:** Absorption and emission spectra were collected for optical characterization. Absorption spectra were measured by a Varian Carry 5000 UV-Vis-NIR Spectrophotometer. Emission spectra were obtained using a NanoLog spectrofluorometer from HORIBA Jobin Yvon. Powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED) and Energy-dispersive X-ray spectroscopy (EDS) were adopted to characterize the size, shape, structure and composition of the synthesized PbS nanoparticles. XRD measurements of nanocrystals were performed by Bruker D8 Advance powder diffractometer, using Cu Kα (λ = 1.54 Å) as the incident radiation. A square wave pulse of 100 Hz was applied during RT measurement, and the voltage of the pulse was varied from 0 V to 10 V. Scanning rate of 0.02° per seconds in 2θ range from 20-70° were employed. Transmission electron microscopy was carried out on JEOL JEM-2010 electron microscopy using 200kV electron source. A drop of as-prepared solution of nanocrystals were placed on a carbon-coated copper grid and dried under air before putting it on to the TEM sample chamber. The film morphology of the nanocrystals and cross-sectional view of the
devices were characterized and analysed on a JEOL field emission scanning electron microscope (JSM-6700F) operating at an accelerating voltage of 5 kV.

![Figure S1](image.png)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak Area</th>
<th>Sigma</th>
<th>k factor</th>
<th>Abs Corr.</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tr>
<td>S K</td>
<td>600</td>
<td>88</td>
<td>1.047</td>
<td>1.000</td>
<td>17.58</td>
<td>2.49</td>
<td>57.96</td>
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<tr>
<td>Pb M</td>
<td>1836</td>
<td>164</td>
<td>1.603</td>
<td>1.000</td>
<td>82.42</td>
<td>2.49</td>
<td>42.04</td>
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<tr>
<td>Totals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
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</tbody>
</table>

**Figure S1.** (a) EDS spectra of 5.5 nm PbS nanocrystals showing the presence of Pb and S atom with intense peak. (b) Elemental analysis table from EDS spectra showing the atomic proportion of Pb and S atoms.
Figure S2. Normalized PL spectrum of different bandgaps PbS nanocrystals. A, B, C and D corresponds for PbS nanocrystals synthesized at 110°C, 120°C, 130°C and 150°C temperatures respectively. The PL of the PbS nanocrystals prepared at 160°C is not presented owing to our measurement range limitations.

Figure S3. TEM images of aggregated PbS nanoparticles prepared at (a) 110°C and (b) 160°C in the absence of HDA, the annealing time was 60 minutes for both these reactions. The procedure was same as for the preparation of PbS nanocrystals only HDA was not used in these reactions. We have carried out the reaction for 60 minutes at 110°C by injecting lead nitrate (0.166g) and thiourea (0.035g) into melted TOPO (2g) only for the first reaction (Figure S5a). For the second reaction we have started the reaction from 110°C then the temperature was increased to 160°C and annealing was carried out for 60 minutes (Figure S5b).

We have measured the size of the nanoparticles from the TEM images. The TEM images show at least greater than 100 nanoparticles (Figure S6e) in a frame, which is much larger for the smaller sized nanocrystals (Figure S6a) in a picture frame of same length. Please note that in the picture frame, the number of bigger sized particles is expectedly less. We have generated histogram of these TEM images for calculating particle size distribution.
Figure S4. TEM images of PbS nanocrystals of size (a) 2.3, (b) 2.7, (c) 3.5, (d) 5.5 and (e) 10 nm respectively. Histograms are showing the nanocrystals size distribution for (a) 2.3 ± 0.18 nm, (b) 2.7 ± 0.19 nm, (c) 3.5 ± 0.23 nm, (d) 5.5 ± 0.25 nm and (e) 10 ± 0.3 nm size respectively. We have used the FWHM of the histogram plot for size dispersion calculation.

We have used the maximum of the absorption spectrum for bandgap energy calculations. One may calculate the band gap from the absorption threshold (Tauc-plot), which is more scientific for band gap calculation. However, the nanocrystals often contain defect states which also may contribute to the absorption spectra, which may shift the actual band edge of the nanocrystals. Thus, a comparison of both will result in the actual picture. We have calculated the bandgap energies using Tauc-plot, which reveals a similar trend, however, with a shift in the energy values towards lower energies (Table S2).

**Table S2.** Bandgap energies calculated from absorption maximum and Tauc-plot of different sized PbS nanocrystals are presented.
Synthesis of TiO$_x$: The TiO$_x$ material was synthesized using sol-gel chemistry following a literature method (S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee1 and A. J. Heeger, *Nat. Photo.*, 2009, 3, 297-303). At first a three-necked flask (100 mL) was heated at 120°C with flowing dry N$_2$ to remove any moisture from inside flask. The sol-gel procedure starts with the injection of the precursor, titanium(IV) isopropoxide (Ti[OCH(CH$_3$)$_2$]$_4$, 5 mL) followed by injection of 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, 20 mL) and ethanolamine (H$_2$NCH$_2$CH$_2$OH, 2 mL) into the three-necked flask connected with a water condenser and nitrogen gas inlet/outlet, one by one at room-temperature (RT). Starting materials must be injected in this order. After one hour stirring at RT, the mixed solution was heated at 80°C for an hour (using a silicon oil bath), followed by heating to 120°C for one hour. During all procedures, the inside of the flask must be under dry N$_2$ atmosphere and the mixed solution must be stirred continuously (magnetic stirring at 600-800 rpm). After heating at 120°C for one hour, the solution transformed to a low-density gel with dark wine color. As a final step after cooling to room temperature, 10 mL of methanol was injected to extract the final transparent TiO$_x$ sol-gel product. To apply on the device, the TiO$_x$ sol-gel product was diluted by 1:500 in methanol. When the TiO$_x$ sol-gel (diluted in methanol) is taken out into air, hydrolysis and condensation start immediately resulting in the formation of Ti-O-Ti linkages. These reactions occur very
slowly because the alcohol solution inhibits contact of the TiO$_x$ with moisture. The hydrolysis and condensation are significantly accelerated, however, after casting to form thin solid films.

**Device Fabrication:** For device fabrication purpose PbS nanocrystals are dispersed in anhydrous octane to produce 15 mg/mL stock solution. Chemical preparation, spin-coating, and post annealing were all done in air. ITO coated glass substrates (Aldrich, 15-25 Ω/sq) were first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. Ethanedithiol in acetonitrile (2% by volume) was first prepared. Spin-coating was carried out in a fume hood with good ventilation. The spin-coater was set at 3000 rpm, 30s duration, and maximized acceleration and deceleration speeds. PbS nanocrystals, 2% EDT solution, anhydrous acetonitrile, and octane used successively throughout the spin-coating process. Each iteration in the layer-by-layer spin casting consisted of four steps: 1$^\text{st}$ PbS nanocrystals octane solution (15 mg/mL), 2$^\text{nd}$ EDT solution [2% (v/v)] for ligand exchange, 3$^\text{rd}$ anhydrous acetonitrile to remove excess EDT and 4$^\text{th}$ anhydrous octane to remove exchanged capping ligands. All these four operations were done correspondingly step by step with spinning. We repeated these steps 12-15 times to obtain smooth and shiny PbS nanocrystals film. And finally the TiO$_x$ precursor solution diluted 1:200 in methanol was spin-casted on top of the PbS nanocrystal layer at the speed 5000 rpm for 60s. The resulting films were ~100-150 nm thick as measured by SEM measurement. Films were stored in vacuum desiccator for overnight and then annealed at 90°C in air for 10 min before the electrode deposition. Then, an aluminium (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of about 1×10$^{-6}$ Torr.
Figure S5. SEM images of spin-coated film surface prepared from 5.5 nm PbS (bandgap = 1.0 eV) nanocrystals before (a) and after (b) EDT treatment.

Figure S6. Photograph of a photovoltaic device prepared using 5.5 nm PbS nanocrystals (bandgap = 1.0 eV) before its characterization, showing transparency and uniformity of the PbS nanocrystals films.

Device Characterization: Current density-voltage (J-V) characteristics of the devices were measured using a Keithley 2420 Source Measure Unit in the dark and under AM1.5G
illumination at 100 mW/cm² supplied by a solar simulator. The J-V measurements were conducted in a vacuum container. The spectral response was measured using a QE/IPCE Measurement Kit (Newport). A dual channel Merlin lock-in amplifier, optical chopper and Si detector is utilized for the sensitive optical power and photocurrent measurements (EQE).

![EQE spectrum](image)

**Figure S7.** EQE (External Quantum Efficiency) or IPCE (Incident Photocurrent to Charge carrier generation Efficiency) spectrum of a device made with 1.5 eV PbS nanocrystals (red triangle symbol), determined by monitoring the photocurrent of the devices at different monochromatic excitations and the absorption spectrum of the 1.5 eV PbS nanocrystals in solution. The EQE spectra obtained from the device was consistent with the solution absorption spectrum with the relative position of the EQE spectrum is slightly red shifted compared to the absorption spectra possibly due to EDT treatment of the PbS nanocrystals film. The maximum IPCE observed for that device is ~8 %. EQE measurements for the other lower bandgap nanocrystals (1.2, 1.0 and 0.6 eV) are not presented owing to the limitation of measurement range up to 1100 nm.