Electronic Supplementary Information

Synthesis of Ternary $Pb_xSn_{1-x}S$ nanocrystals with Tunable Band Gap

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Experimental Section

I. Materials.

All of the chemical reagents and solvents were used without further purification. Lead oxide (PbO, >99%), stannous oxide (SnO, >90%), sulfur powder (S, >99.5%), oleic acid (OA, 90%), oleylamine (OLA, 70%) and 1-octadecene (ODE, 90%) were purchased from Aladdin and employed as received.

II. The typical synthesis of $Pb_xSn_{1-x}S$ nanocrystals.

15 mL oleic acid, 15 mL 1-octadecene and 4 mmol mixture of stannous oxide and lead oxide were added to a 100 mL two-neck flask followed with vacuum pumping and N_2 bubbling. Then the solution was kept at 250 □ for 1 h. Meanwhile, 30 mL oleylamine and 4 mmol sulfur were added to a 100 mL two-neck flask followed with vacuum pumping and N_2 bubbling and kept at 60 □ for 1 h. The OLA/S solution was rapidly injected into the first flask when it was completely dissolved. The temperature was then raised to 270 □ and kept for the range of 100 seconds to 600 seconds under vigorous stirring to obtain the nanocrystals of different sizes. The product was purified by standard polar/nonpolar solvent precipitation technique, using a high-speed centrifuge.

III. The synthesis of PbS nanocrystals.

15 mL oleic acid, 15 mL 1-octadecene and 4 mmol lead oxide were added to a 100 mL two-neck flask followed with vaccum pumping and N_2 bubbling. Then heat the solution to 250 □ and kept for 1 h. About 4 mmol sulfur powder and 30 mL oleylamine were added to another 100 mL two-flask with vaccum pumping and N_2 bubbling and kept under 60 □ for 1 h. The OLA/S solution was rapidly inject into the first flask when it was completely dissolved. The temperature was then raised to 270 □ and kept for the range of 100 seconds to 600 seconds under vigorous stirring. The product was purified by standard polar/nonpolar solvent precipitation technique, using a high-speed centrifuge.

IV. The synthesis of SnS nanocrystals.

15 mL oleic acid, 15 mL 1-octadecene and 4 mmol stannous oxide were added to a 100 mL two-neck flask followed with vaccum pumping and N_2 bubbling. Then heat the solution to 250 □ and kept for 1 h. About 4 mmol sulfur powder and 30 mL oleylamine were added to another 100 mL two-flask with vaccum pumping and N_2 bubbling and kept under 60 □ for 1 h. The OLA/S solution was rapidly inject into the first flask when it was completely dissolved. The temperature was then raised to 270 □ and kept for the range of 100 seconds to 600 seconds under vigorous stirring. The product was purified by standard polar/nonpolar solvent precipitation technique, using a high-speed centrifuge.

V. Structural and optical characterization.

The Oxford INCA energy-dispersive X-ray spectroscopy (EDS) detector was utilized for analysis of the element composition and proportion. The crystal structure of PbSnS nanocrystals was characterized by powder X-ray diffraction (XRD) using Cu kα radiation (λ=1.54 Å). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were taken by using a JEM 2100 microscope at 200 kV accelerating voltage. A Lambda 20 UV-vis spectrometer was also used to carry out UV-vis absorption spectra to measure the optical properties of PbSnS nanocrystals.

Table. S1 Chemical composition of PbSnS nanocrystals determined from EDS analysis

		Atomic (%)		
Serial	Pb/(Pb+Sn)	Pb	Sn	S
I	0.54	22.85	19.47	57.68
II	0.62	30.76	18.86	50.38
III	0.66	30.63	15.78	53.59
IV	0.71	30.83	12.59	56.58
V	0.80	38.30	9.58	52.12
VI	0.85	39.40	6.95	53.65

Table. S1 shows the chemical stoichiometries of seven SnSSe samples measured by an EDS detector. The whole samples have an Pb/(Pb+Sn) ratio of 0.54, 0.62, 0.66, 0.71, 0.80 and 0.85. Considering the ±2% uncertainty in the elemental composition data analyzed by EDS, the average compositions of the nanocrystals for the six samples calculated from **Table. S1** are $Pb_{0.54}Sn_{0.46}S$, $Pb_{0.62}Sn_{0.38}S$, $Pb_{0.66}Sn_{0.34}S$, $Pb_{0.71}Sn_{0.29}S$, $Pb_{0.80}Sn_{0.20}S$, $Pb_{0.85}Sn_{0.15}S$, respectively.

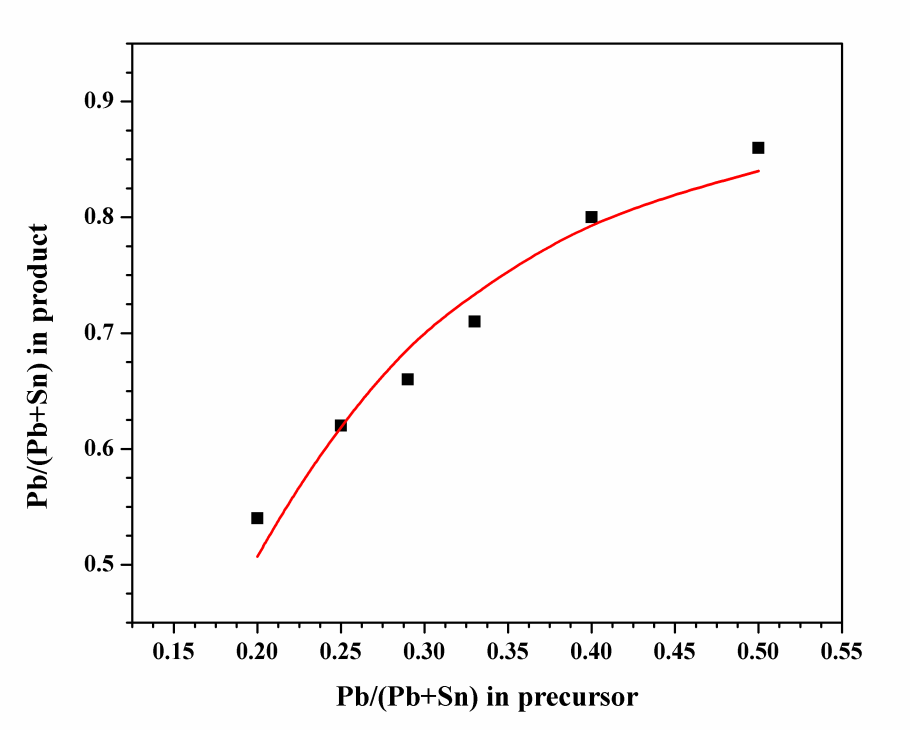

Fig. S1 EDS is used to measure the relative amount of lead in the product *versus* the relative amount of lead in the precursor solution.

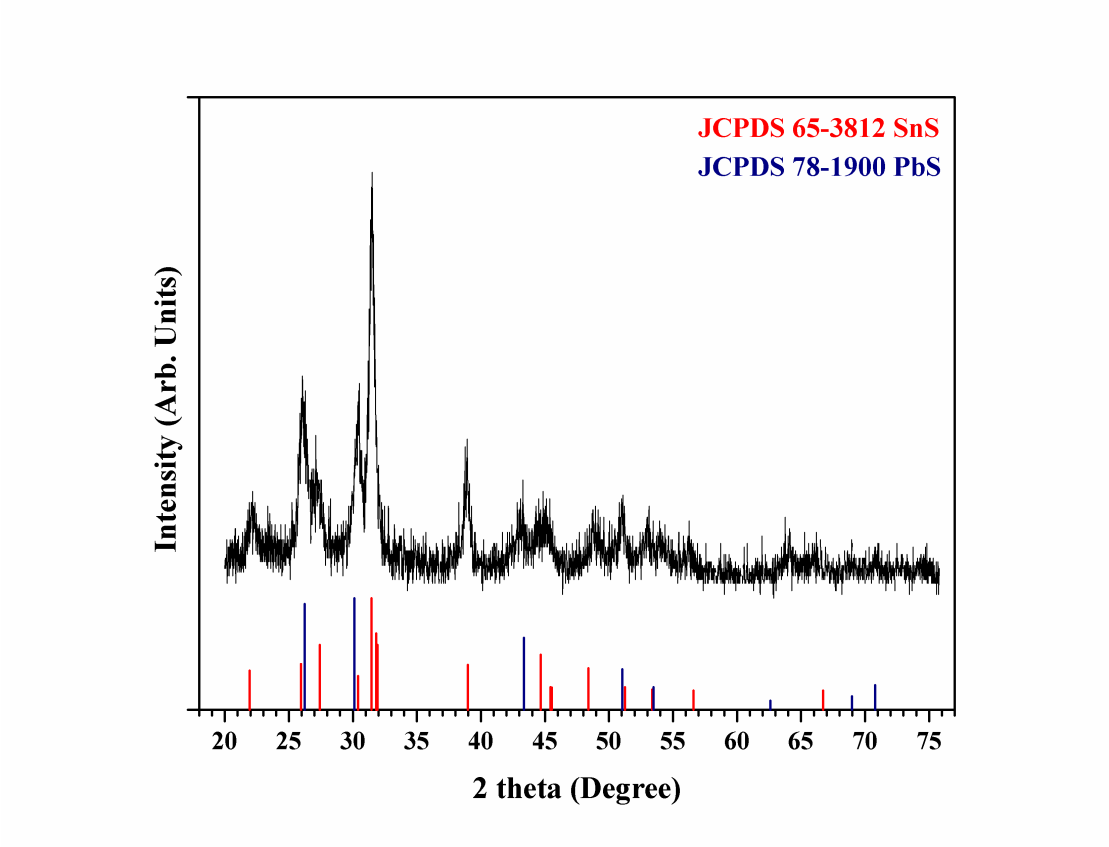

Fig. S2 PbSnS nanocrystals sample with a secondary phase SnS (JCPDS 65-3812).

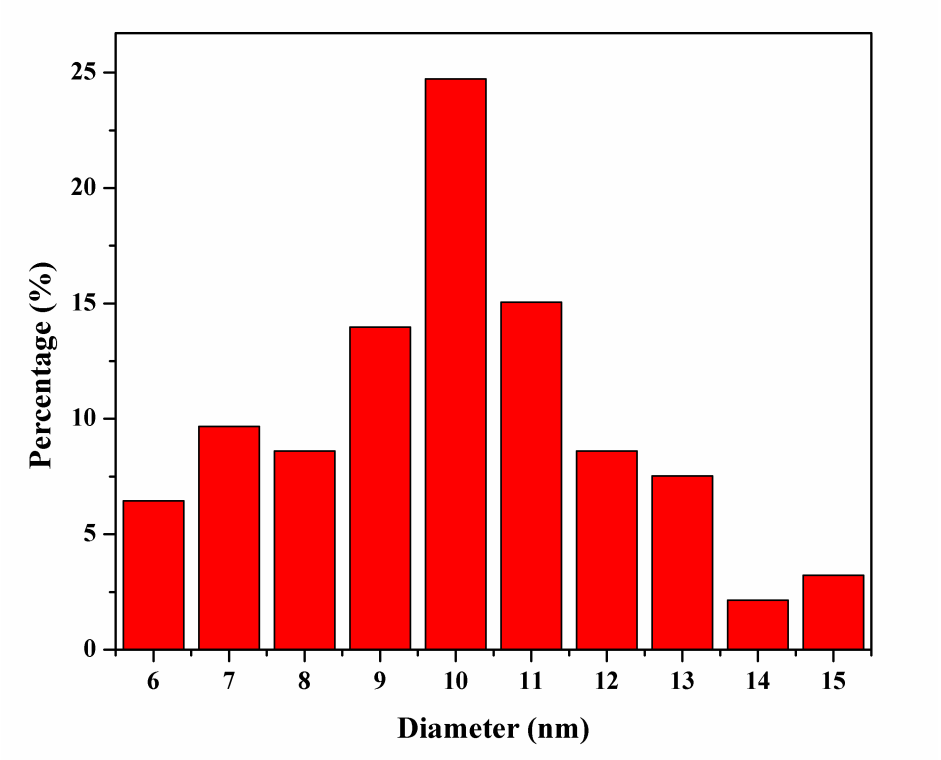

Fig. S3 Histogram of nanoparticle size distribution of PbSnS nanocrystals (x=0.85).

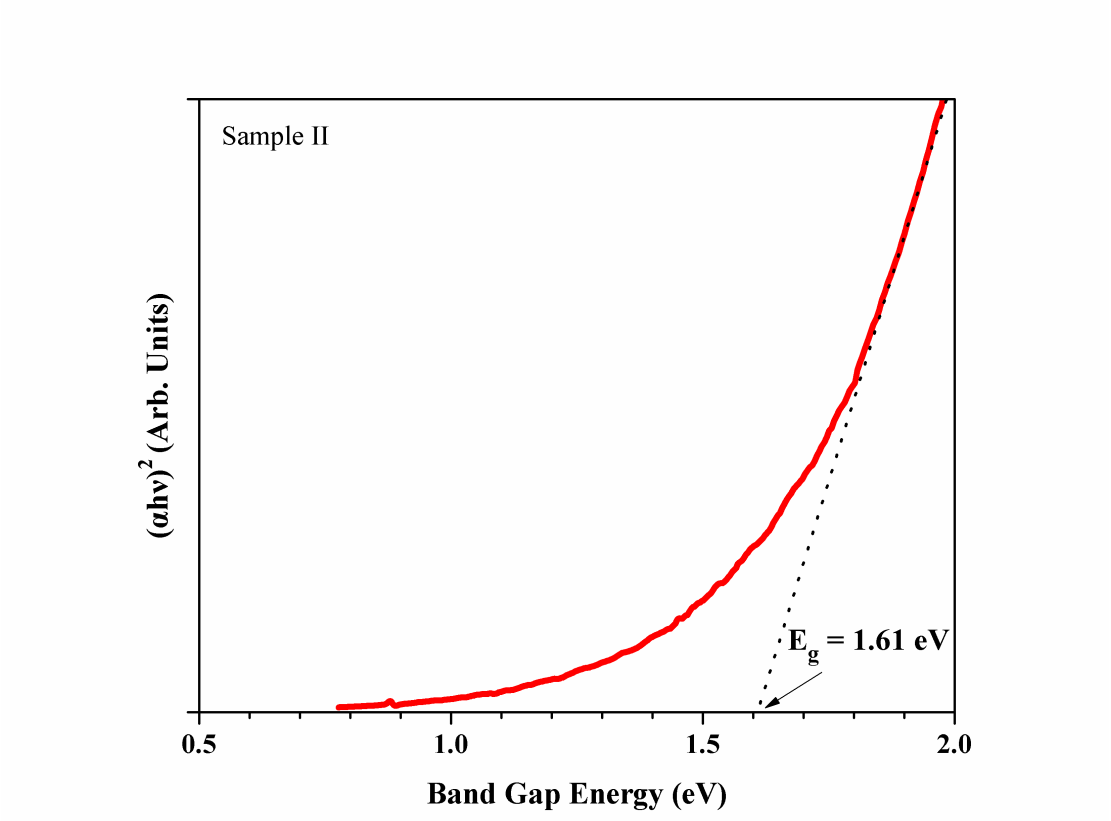

Fig. S4 Obtained band gap energies of Sample VI.

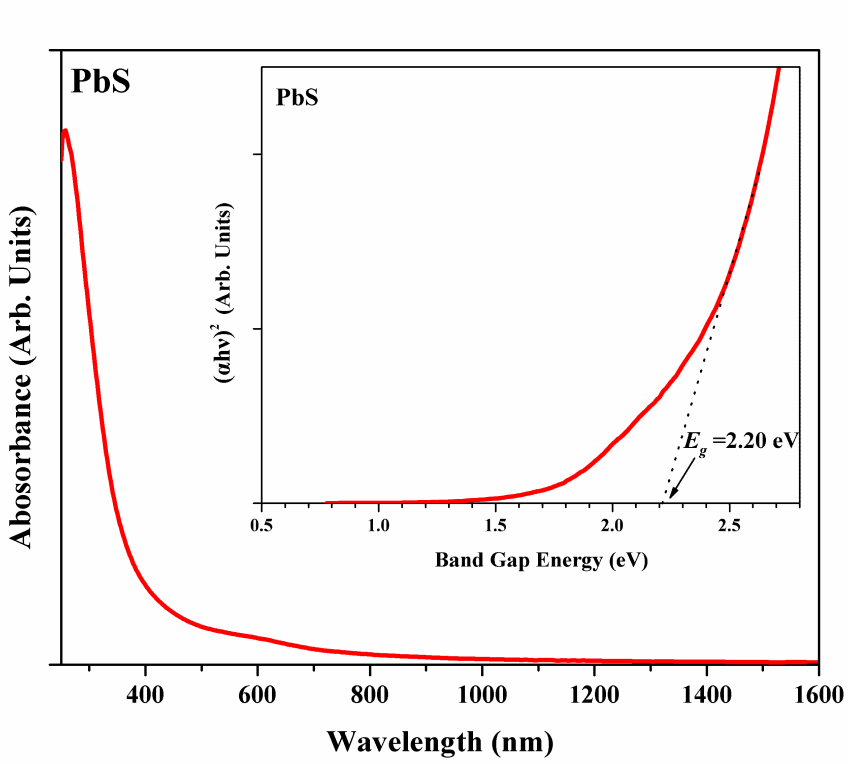

Fig. S5 Abosorbance spectra of PbS nanocrystals and the obtained band gap energy (inset).