Supporting Information

Organometallic Synthesis, Structure Determination, Shape Evolution and Formation Mechanism of Hexapod-like Ternary $PbSe_xS_{1-x}$ Nanostructures with Tunable Compositions

Genrong Shao,[†,‡,§,//] Guihuan Chen,[†,‡,§,//] Jian Zuo,[†] Ming Gong,[⊥] and Qing Yang[*,†,‡,§,//]

[†] Hefei National Laboratory of Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, Anhui, P. R. China.

[‡] Department of Chemistry, University of Science and Technology of China, Hefei 230026, Anhui, P. R. China.

[§] Laboratory of Nanomaterials for Energy Conversion, University of Science and Technology of China, Hefei 230026, Anhui, P. R. China.

[//] Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei 230026, Anhui, P. R. China

[⊥] Experiment Center of Engineering and Materials Science, University of Science and Technology of China, Hefei 230027, Anhui, P. R. China.

E-mail: qyoung@ustc.edu.cn; Fax: +86-551-63606266; Tel: +86-551-63600243.

MATERIALS AND METHODS

Materials

Dibenzylamine (DBA, analytical grade, 99%) and lead (II) acetate trihydrate ($Pb(CHCOO)_2 \cdot 3H_2O$) were purchased from Alfa Aesar. Oleic acid (OA) was purchased from Shanghai Chemical Reagents Co. China. Triphenylphosphine selenide (Ph_3PSe) and dibenzyl disulfide (DBDS) were purchased from TCI. All the chemicals were used as obtained without further purification.

Methods

All manipulations were carried out using standard Schlenk techniques under argon flow. In the current work, the growth of the $PbSe_xS_{1-x}$ nanostructures including two end members of PbS and PbSe is performed via an organometallic synthetic route from the reactions of Pb(II) acetate trihydrate with Ph_3PSe and/or DBDS in DBA with the addition of OA at 260 °C for 5 min, which is adopted with variations from our recent work for the preparation of PbSe nanostructures from reaction of tetraphenyl lead (Ph_4Pb) with Ph_3PSe in DBA in the presence of OA and oleylamine (OAm) at 220 °C for 30 min.[S1]

Preparation of Sulfur-precursor Solution.

0.075 mmol of DBDS was dissolved into 1.0 mL of DBA in a 10 mL container and formed a transparent solvent after ultrasound for 5 minutes and then kept at 70°C for further use.

Synthesis of Hexapod-like Ternary $PbSe_xS_{1-x}$ Nanocrystals.

Hexapod-like ternary $PbSe_xS_{1-x}$ nanocrystals with tunable compositions were synthesized via the organometallic route under argon atmosphere. The preheated sulfur precursor was injected into reaction solution at 260 °C where lead and selenium precursors have been already involved at room

temperature and carried out at temperatures rising from 150 to 260 °C for the growth of the ternary $PbSe_xS_{1-x}$ nanostructures with varied compositions. For short, we use x, the mole ratio of Se precursor in feedstock, to designate the actual concentration of the grown samples for instead for easy discussion. In a typical synthesis, 0.25 mmol of lead(II) acetate trihydrate and 0.1 mmol of Ph_3PSe were added into 100 mL of three-necked flask containing 4.25 mL of DBA and 0.75 mL of OA and magnetically stirred under a flow of argon. The mixture was heated to 150 °C at a rate of 10 °C/min and kept at that temperature for 30 min to remove the moisture and oxygen, and then was heated to 260 °C in 6 min. Upon heated, reaction system turned from light-yellow (the color of oleic acid) to light black, resulting the formation of small PbSe crystal nucleus immediately. When the temperature arrived at 260 °C for 5 seconds, the as-prepared sulfur precursor (0.075 mmol of DBDS) in 1.0 mL of DBA preheated at 70 °C was rapidly injected into the above hot solution and the mixture turned to black immediately, indicating the formation of the aimed products. 5 minutes later, the dark mixture was cooled to room temperature rapidly by removing the heating source promptly and 5.0 mL of toluene was added into reaction system. The crude product was separated via centrifugation (9000 rpm, 4 min and three times) and dried at 60 °C in air for further characterizations. Some more experiments were systematically carried out with similar procedures for the preparation of the other ternary $PbSe_xS_{1-x}$ nanocrystals with the variation of mole ratio (x) in feedstocks and reaction conditions.

Synthesis of Hexapod-like Binary PbSe Nanocrystals.

In a typical synthesis, 0.25 mmol of lead (II) acetate trihydrate and 0.25 mmol of Ph_3PSe were added into 100 mL of three-necked flask containing 4.25 mL of DBA and 0.75 mL of OA and magnetically stirred under a flow of argon. The heating procedure was performed as the same as that for the ternaries as described above. When the temperature arrived at 260 °C for 5 seconds,

what injected into the solutions was not the sulfur precursor but only 1 mL of DBA used for instead, as compared to the synthesis for the ternary $PbSe_xS_{1-x}$ nanocrystals. The resulted binary PbSe nanocrystals were washed and filtered as described above and dried at 60 °C in air for further characterization.

Synthesis of Hexapod-like Binary PbS Nanocrystals.

In a typical synthesis, 0.25 mmol of lead(II) acetate trihydrate was added into 100 mL of three-necked flask containing 4.25 mL DBA and 0.75 mL of OA and magnetically stirred under a flow of argon. The heating procedure was performed as the same as that for the ternaries as described above. When the temperature arrived at 260 °C for 5 seconds, the as-prepared sulfur precursor with 0.125 mmol of DBDS in 1.0 mL of DBA was rapidly injected into the above hot solution and reacted further for 5 min. The resulted binary PbS nanocrystals were washed and filtered as described above and dried at 60 °C in air for further characterization.

Characterizations.

The samples were characterized by different analytic techniques. The morphologies of the products were observed by scanning electron microscope (SEM, JSM-6700F), and transmission electron microscope (TEM, Hitachi H-7650). The structure and microstructure of the as-prepared samples were determined by X-ray powder diffraction (XRD, on a Philips X'pert PRO X-ray diffractometer, Cu Kα, λ = 1.54182 Å), high resolution TEM (HRTEM, a JEOL-2010 transmission electron microscope), and selected-area electron diffraction (SEAD) attached to the HRTEM. Meanwhile, the samples were also checked by Raman spectroscopy, tested on a JYLABRAM-HR confocal laser micro-Raman spectrometer with 514.5 nm at room temperature and low temperatures (-190 °C). The compositions of the samples were investigated by energy dispersive X-ray spectroscopy (EDX, OXFORD INCA system), high-angle annular dark-field imaging in the

scanning TEM (HAADF-STEM), electron energy loss spectroscopic (EELS), and X-ray photoelectron spectroscopy (XPS, an ESCALab MKII X-ray photo-electron spectrometer using Mg Ka radiation exciting source).

Table S1. Lattice parameters calculated from XRD detections and compositions determined by EDX and XPS for the ternary $PbSe_xS_{1-x}$ nanostructures including two extremes of binary end members of PbS and PbSe obtained in 5.75 mL of DBA with 0.25 mL of OA in the reaction system.

Norminal compositions	XRD results	EDX results			XPS results	
	Lattice constants a (Å)	Pb/(Se+S)	x	1-x	x	1-x
PbS	5.919	55.14 : 44.86				
$PbSe_{0.1}S_{0.9}$	5.952	55.70 : 44.30	0.260	0.740	0.093	0.907
$PbSe_{0.2}S_{0.8}$	6.004	55.12 : 44.88	0.485	0.515	0.187	0.813
$PbSe_{0.4}S_{0.6}$	6.011	55.76 : 44.24	0.606	0.394	0.282	0.718
$PbSe_{0.5}S_{0.5}$	6.038	55.24 : 44.76	0.730	0.270	0.349	0.651
$PbSe_{0.6}S_{0.4}$	6.049	55.18 : 44.82	0.752	0.248	0.454	0.546
$PbSe_{0.8}S_{0.2}$	6.082	54.60 : 45.40	0.920	0.080	0.536	0.464
$PbSe_{0.9}S_{0.1}$	6.087	54.52 : 45.48	0.952	0.048	0.611	0.389
PbSe	6.125	55.49 : 44.51				

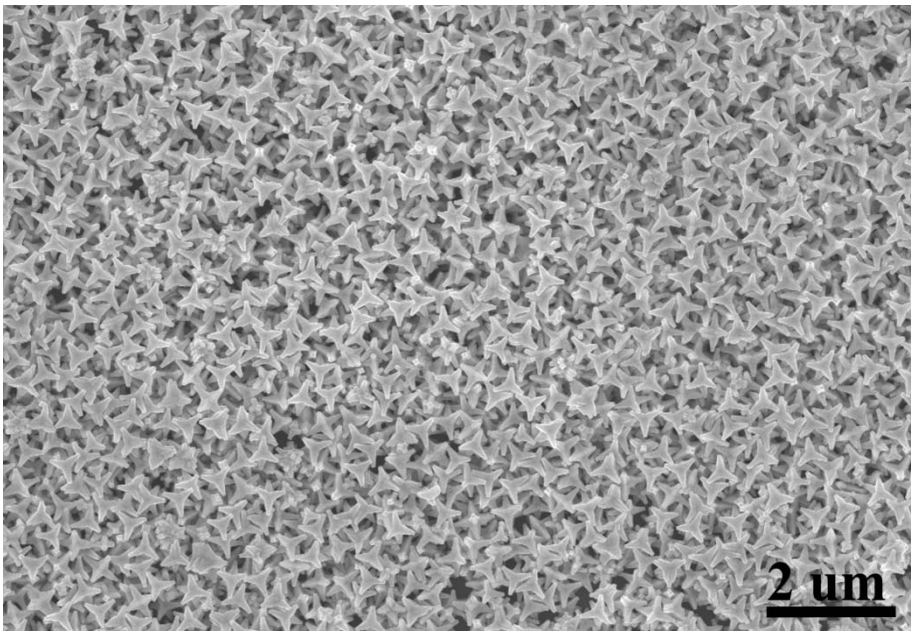


Figure S1. A typical large-scale SEM image for the hexapod-like ternary $PbSe_xS_{1-x}$ (x = 0.4) nanostructures obtained from the reaction of Pb(II) salt with triphenylphosphine selenide (Ph_3PSe) and dibenzyl disulfide (DBDS) in dibenzylamine (DBA) with the addition of oleic acid (OA) in DBA (5.25 mL) with 0.75 mL of OA at 260 °C for 5 min in the reaction systems.

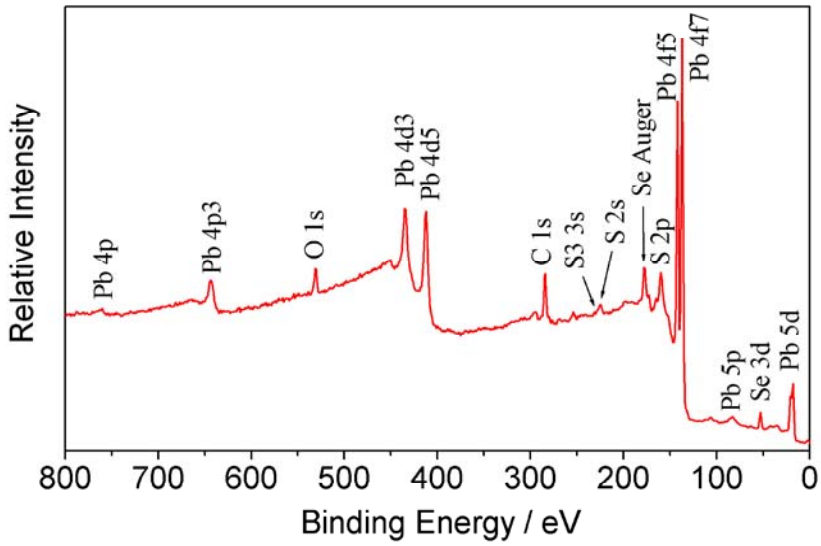


Figure S2. XPS spectra of the hexapod-like ternary $PbSe_xS_{1-x}$ (x = 0.4) nanostructures obtained in 5.25 mL of DBA with addition of 0.75 mL of OA in the reaction system.

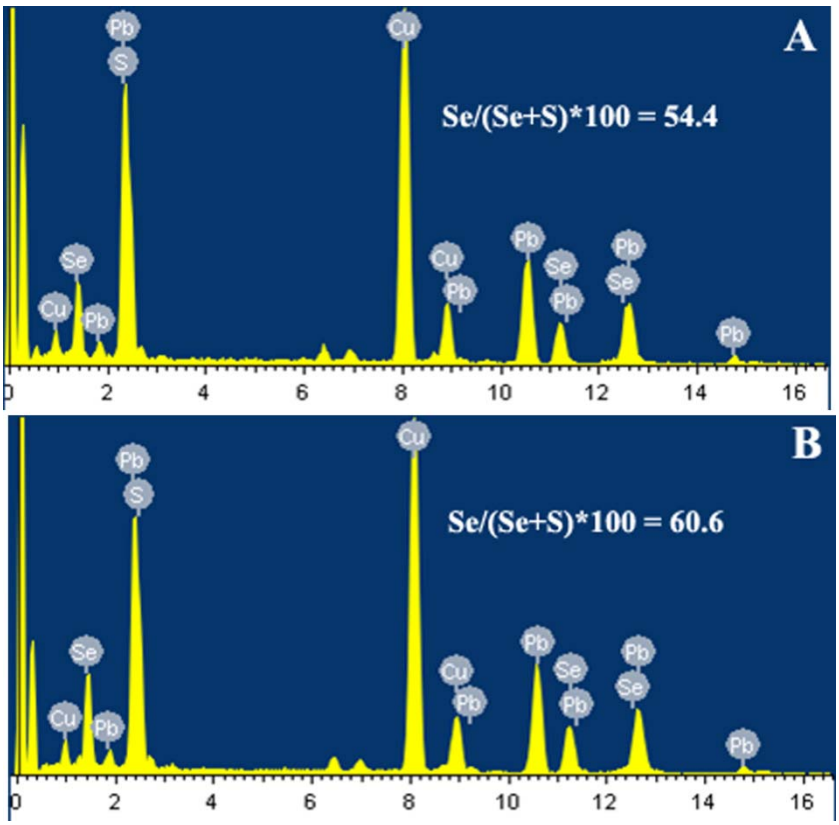


Figure S3. EDX spectra of a typical hexapod-like $PbSe_xS_{1-x}$ (x = 0.4) nanostructure obtained in 5.25 mL of DBA with addition of 0.75 mL of OA: (A) Measured on the tip of an arm, and (B) the entire individual hexapod.

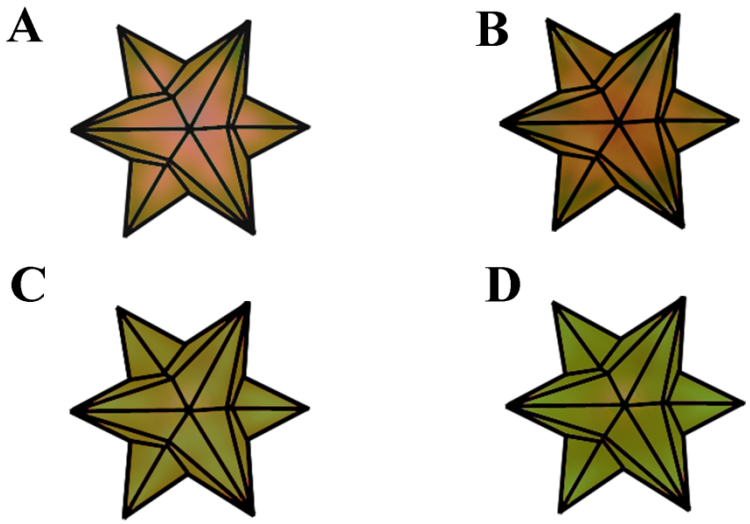


Figure S4. Schematic models to illustrate the ideal characteristics of the microstructure for the ternaries with varied composition. (A) – (D) are the corresponding models for the ternaries with x

values set as 0.2, 0.4, 0.6 and 0.8, respectively, shown in Figure 5.

Table S2. Lattice parameters calculated from XRD detections and compositions determined by EDX and XPS for the ternary $PbSe_xS_{1-x}$ nanostructures including two extremes of binary end members of PbS and PbSe obtained in 5.75 mL of DBA with 0.25 mL of OA in the reaction system.

Norminal	XRD results	EDX results		XPS results	
compositions	Lattice constants a (Å)	x	1-x	x	1-x
PbS	5.915				
$PbSe_{0.1}S_{0.9}$	5.916	0.170	0.830	0.084	0.916
$PbSe_{0.2}S_{0.8}$	5.938	0.311	0.689	0.104	0.896
$PbSe_{0.4}S_{0.6}$	5.992	0.461	0.539	0.232	0.768
$PbSe_{0.5}S_{0.5}$	6.008	0.556	0.434	0.328	0.672
$PbSe_{0.6}S_{0.4}$	6.048	0.612	0.388	0.420	0.580
$PbSe_{0.8}S_{0.2}$	6.059	0.812	0.188	0.532	0.468
$PbSe_{0.9}S_{0.1}$	6.082	0.840	0.160	0.588	0.412
PbSe	6.101				

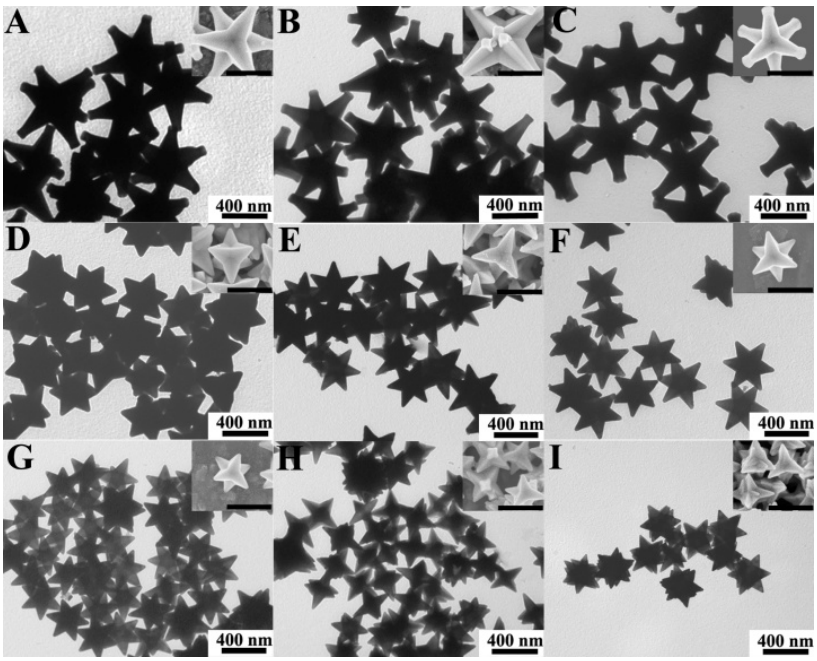


Figure S5. TEM images of the hexapod-like ternary $PbSe_xS_{1-x}$ nanostructures obtained at 260 °C

for 5 min in DBA (5.75 mL) with 0.25 mL of OA in the reaction systems with x changing from 0 to 1, respectively. (A) x = 0, (B) x = 0.1, (C) x = 0.2, (D) x = 0.4, (E) x = 0.5, (F) x = 0.6, (G) x = 0.8, (H) x = 0.9, and (I) x = 1.0. Insets are the corresponding SEM images. Scale bars in the insets are 400 nm.

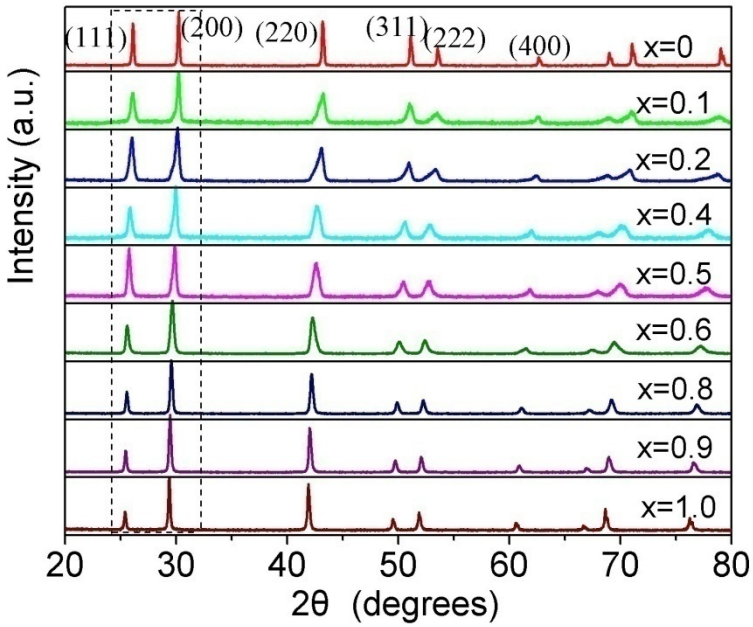


Figure S6. XRD patterns of the hexapod-like ternary $PbSe_xS_{1-x}$ nanostructures including two extremes of binary end members of PbS (x = 0) and PbSe (x = 1.0) obtained in 5.75 mL of DBA with 0.25 mL of OA in the reaction system.

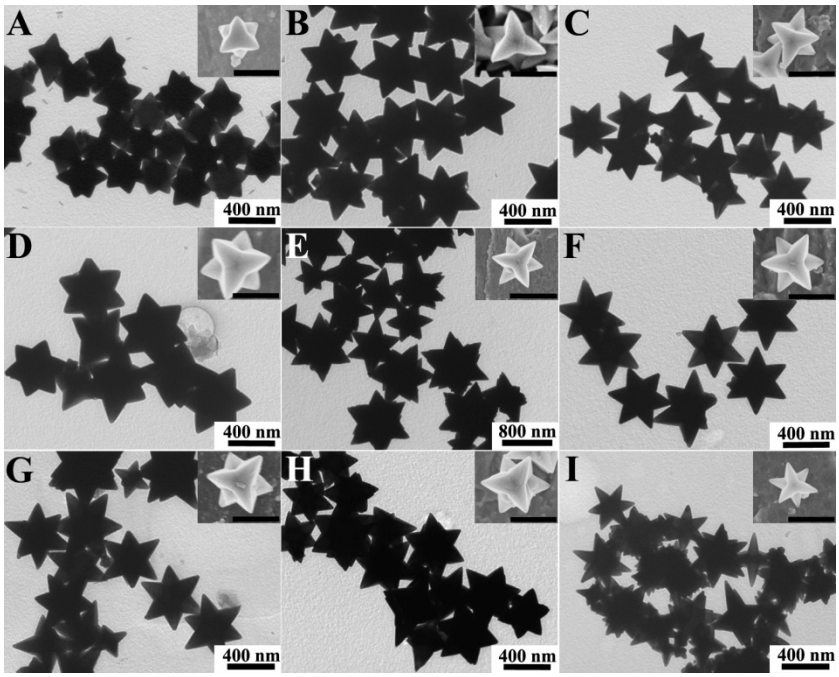


Figure S7. TEM images of the hexapod-like ternary $PbSe_xS_{1-x}$ nanostructures obtained at 260 °C for 5 min in DBA (4.5 mL) with 1.5 mL of OA in the reaction systems with x changing from 0 to 1.0, respectively. (A) x = 0, (B) x = 0.1, (C) x = 0.2, (D) x = 0.4, (E) x = 0.5, (F) x = 0.6, (G) x = 0.8, (H) x = 0.9, and (I) x = 1.0. Insets are the corresponding SEM images. The scale bars in the insets are 400 nm except for the one in (E) is 800 nm.

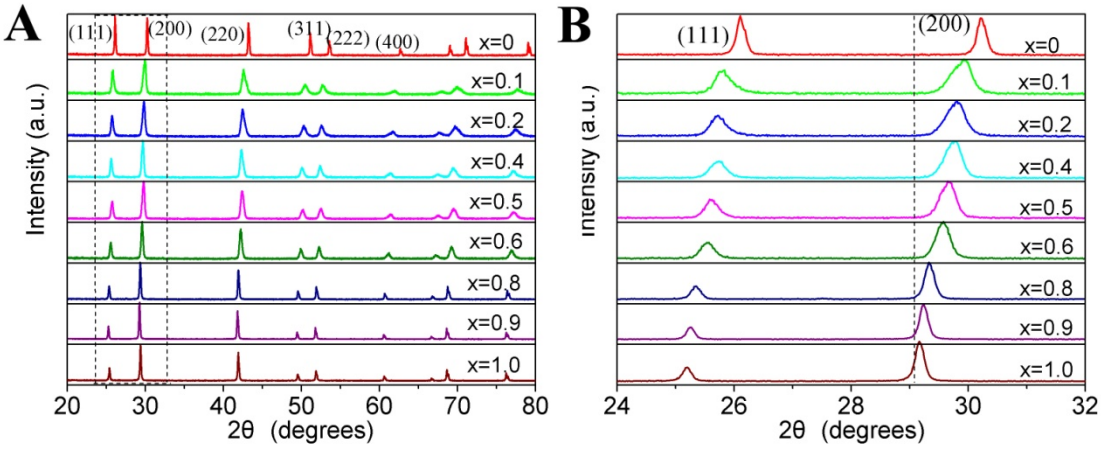


Figure S8. (A) XRD patterns of the hexapod-like ternary $PbSe_xS_{1-x}$ nanostructures including two extremes of binary end members of PbS (x = 0) and PbSe (x = 1.0) obtained in 4.5 mL of DBA with

1.5 mL of OA, and (B) expanded view for the rectangle in (A), showing systematical shifts of (111) and (200) diffraction peaks. Dashed line in (B) is a guide to the shifts.

Table S3. Lattice parameters calculated from XRD detections and compositions determined by EDX and XPS for the ternary $PbSe_xS_{1-x}$ nanostructures including two extremes of binary end members of PbS and PbSe obtained in 4.5 mL of DBA with 1.5 mL of OA in the reaction system.

Norminal compositions	XRD results	EDX results		XPS results	
	Lattice constants a (Å)	x	1-x	x	1-x
PbS	5.922				
$PbSe_{0.1}S_{0.9}$	6.007	0.463	0.537	0.168	0.832
$PbSe_{0.2}S_{0.8}$	6.027	0.570	0.430	0.230	0.770
$PbSe_{0.4}S_{0.6}$	6.029	0.670	0.330	0.303	0.697
$PbSe_{0.5}S_{0.5}$	6.045	0.770	0.230	0.318	0.682
$PbSe_{0.6}S_{0.4}$	6.058	0.779	0.221	0.367	0.633
$PbSe_{0.8}S_{0.2}$	6.097	0.920	0.080	0.453	0.547
$PbSe_{0.9}S_{0.1}$	6.112	0.966	0.034	0.470	0.530
PbSe	6.130				

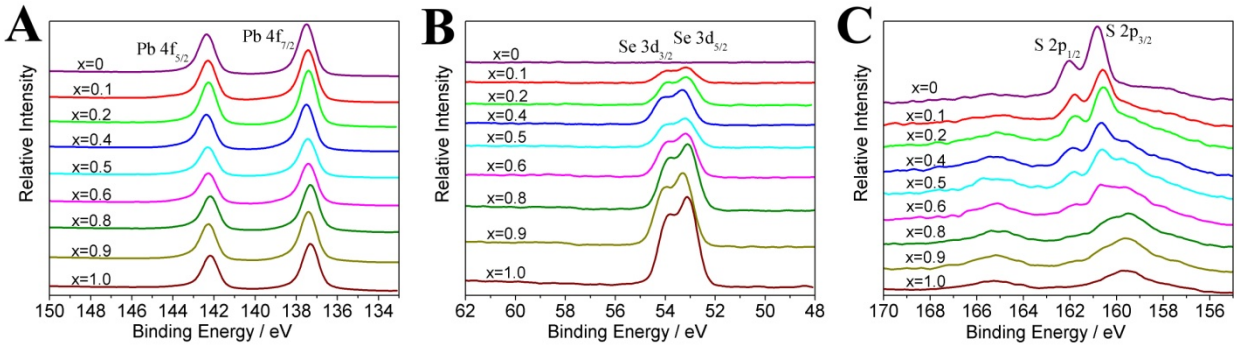


Figure S9. XPS spectra of the hexapod-like ternary $PbSe_xS_{1-x}$ nanostructures including two extremes of binary end members of PbS (x = 0) and PbSe (x = 1.0) obtained in 4.5 mL of DBA with 1.5 mL of OA in the reaction system. (A) Pb, (B) Se and (C) S close-up spectra, respectively.

Table S4. Lattice parameters calculated from XRD detections and compositions determined by EDX and XPS for the ternary $PbSe_xS_{1-x}$ (x = 0.4) nanostructures with addition of different amount of OA into the reaction system. The gray lines are selectively adopted from Table S1-3.

Amount of OA	XRD results	EDX results		XPS results	
	Lattice constants a (Å)	x	1-x	x	1-x
0.25 mL	5.992	0.461	0.539	0.232	0.768
0.50 mL	5.994	0.514	0.486	0.272	0.728
0.75 mL	6.011	0.606	0.394	0.282	0.718
1.0 mL	6.020	0.745	0.255	0.309	0.691
1.5 mL	6.029	0.758	0.242	0.303	0.697
2.5 mL	6.084	0.816	0.184	0.358	0.642

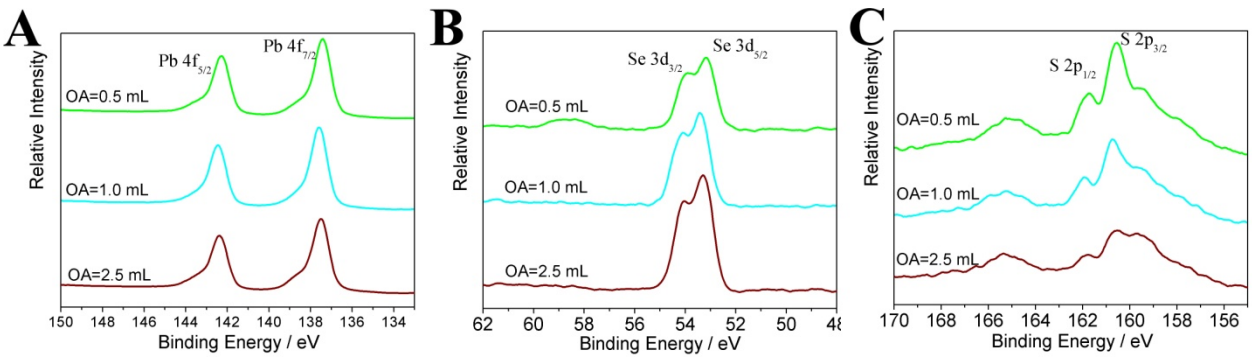


Figure S10. XPS spectra of the as-synthesized hexapod-like ternary $PbSe_xS_{1-x}$ samples prepared under additional various amount of OA (0.5, 1.0 and 2.5 mL) with x values fixed at 0.4 in the feedstock: (A) Pb, (B) Se and (C) S close-up spectra, respectively.

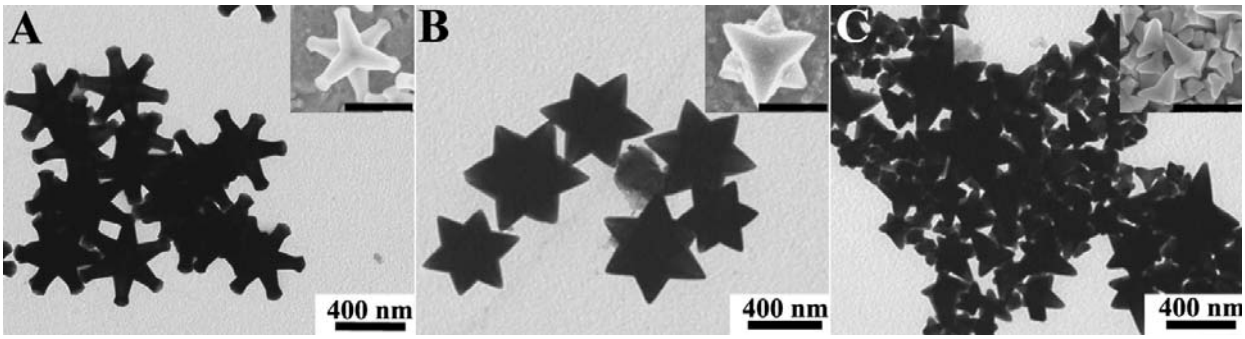


Figure S11. TEM images showing morphologies evolution of the hexapod-like ternary $PbSe_xS_{1-x}$ (x = 0.4) obtained by adding various amount of OA: (A) 0.5, (B) 1.0 and (C) 2.5 mL, respectively.

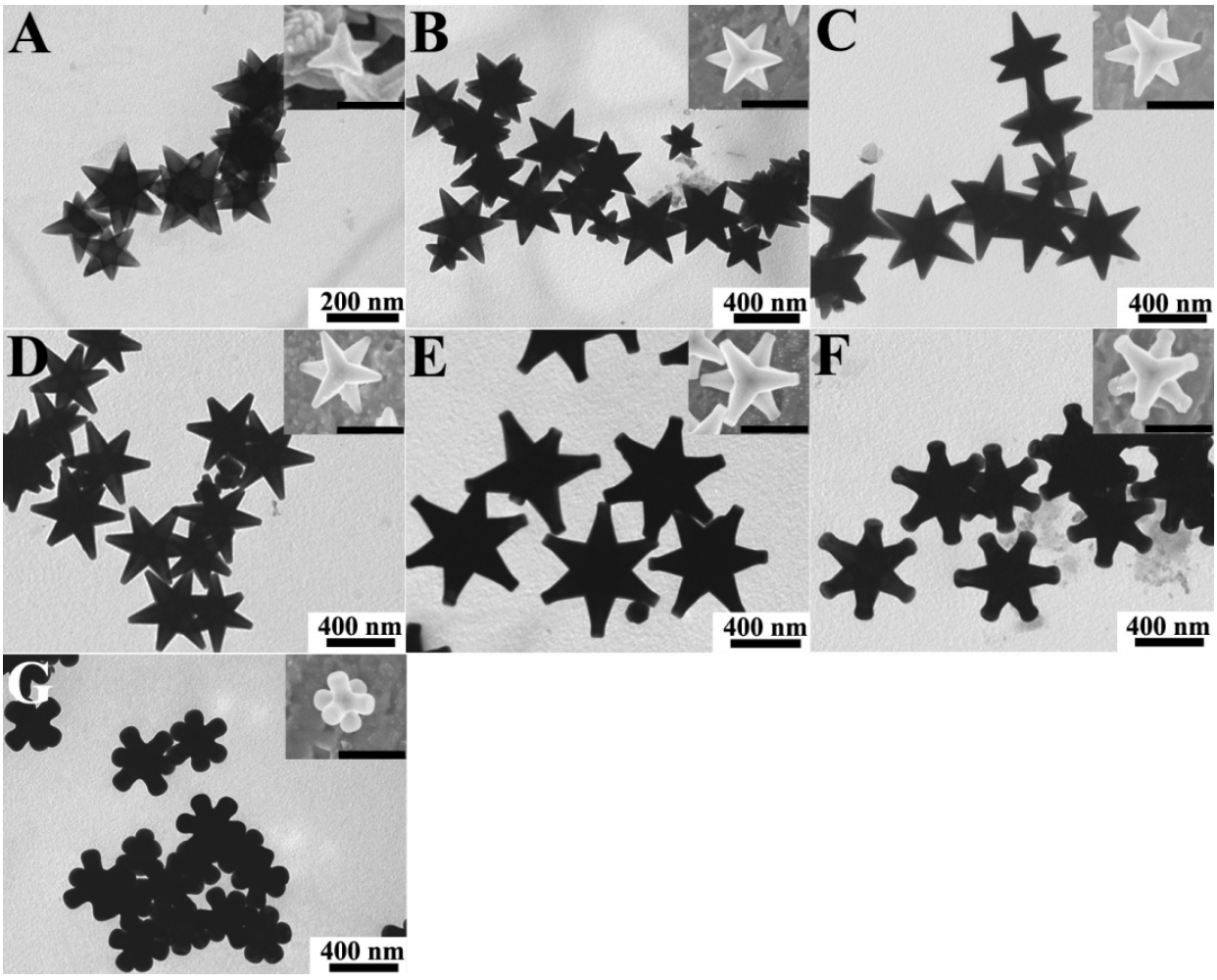
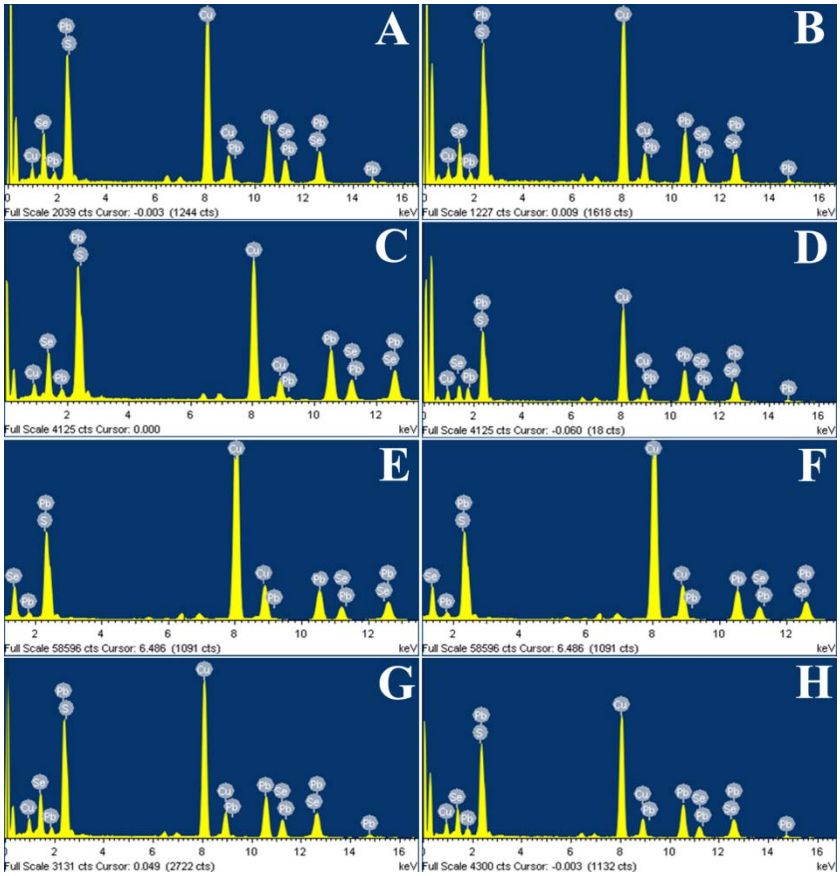


Figure S12. TEM images showing morphologies evolution of the hexapod-like ternary $PbSe_xS_{1-x}$ (x = 0.4) obtained at different reaction time. (A) 1, (B) 2, (C) 3, (D) 4, (E) 10, (F) 30 and (G) 60 min, respectively. The scale bars in insets are 400 nm except for the one in (A) is 200 nm.



Se mole ratio (%)	5 min	10 min	30 min	60 min
entire hexapod	60.6	59.7	59.0	59.9
tip area	54.4	58.5	58.6	59.3

Figure S13. EDX spectra of the hexapod-like ternary $PbSe_xS_{1-x}$ (x = 0.4) nanostructures for different regions with different reaction time from 5 to 60 minutes: (A) 5, (C) 10, (E) 30 and (G) 60 min for a whole individual hexapod, respectively; (B) 5, (D) 10, (F) 30 and (H) 60 min from a tip (area) in the singular hexapod, respectively. The Cu signals originate from the substrate of copper grids. The table shown under the EDX spectra presents the detailed detections of the actual Se mole ratio in the $PbSe_xS_{1-x}$ (x = 0.4) ternaries with the variation of reaction time by EDX.

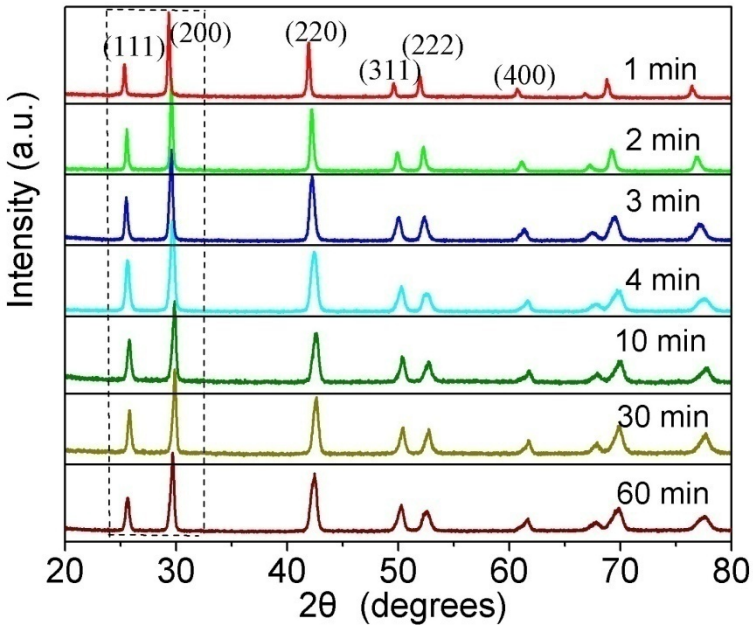


Figure S14. XRD patterns of the hexapod-like ternary $PbSe_xS_{1-x}$ (x = 0.4) nanocrystals obtained for different reaction time.

Table S5. Lattice parameters calculated from XRD detections and compositions determined by EDX and XPS for the ternary $PbSe_xS_{1-x}$ (x = 0.4) nanostructures. The gray line is selectively adopted from Table S1.

Reaction time	XRD results	EDX results		XPS results	
	Lattice constants a (Å)	x	1-x	x	1-x
1 min	6.096	0.960	0.004	0.869	0.131
2 min	6.058	0.800	0.200	0.668	0.332
3 min	6.053	0.652	0.348	0.491	0.509
4 min	6.019	0.615	0.385	0.332	0.668
5 min	6.011	0.606	0.394	0.282	0.718
10 min	6.010	0.597	0.403	0.332	0.668
30 min	6.004	0.590	0.410	0.317	0.683
60 min	6.000	0.599	0.401	0.328	0.672

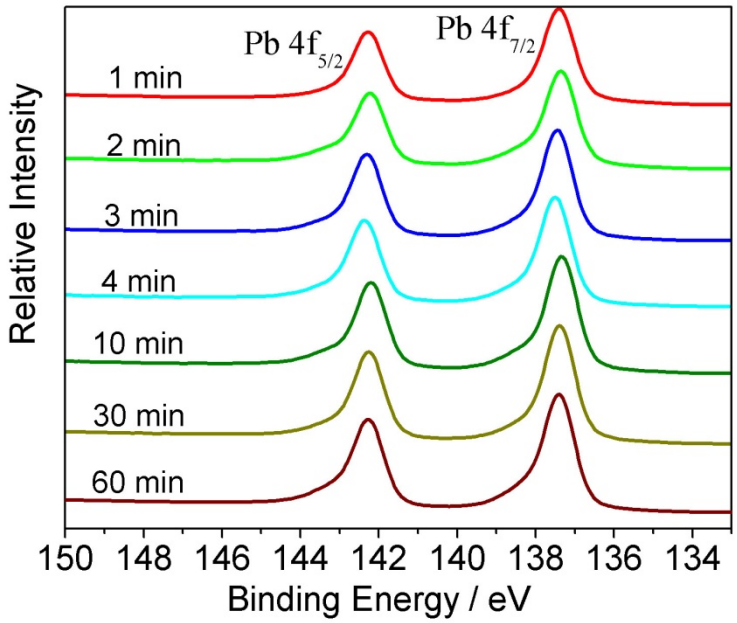


Figure S15. Pb close-up XPS spectra of the hexapod-like ternary $PbSe_xS_{1-x}$ (x = 0.4) nanocrystals prepared at different reaction time.

References.

S1. Shao, G. R.; Chen, G. H.; Yang, W. L.; Ding, T.; Zuo, J.; Yang, Q., Organometallic-Route Synthesis, Controllable Growth, Mechanism Investigation, and Surface Feature of PbSe Nanostructures with Tunable Shapes. *Langmuir* **2014,** 30 (10), 2863-2872.